

C. State Plans for New Source Review for Nonattainment Purposes

Section 51.18 of Title 40 of the Code of Federal Regulations is amended as follows:

1. By adding a new paragraph (j)(1)(iv)(c) to read as follows: "(c) The fugitive emissions of a stationary source shall not be included in determining for any of the purposes of this subsection whether it is a major stationary source, unless the source belongs to one of the following categories of stationary sources:

- (1) Coal cleaning plants (with thermal dryers);
- (2) Kraft pulp mills;
- (3) Portland cement plants;
- (4) Primary zinc smelters;
- (5) Iron and steel mills;
- (6) Primary aluminum ore reduction plants;
- (7) Primary copper smelters;
- (8) Municipal incinerators capable of charging more than 250 tons of refuse per day;
- (9) Hydrofluoric, sulfuric, or nitric acid plants;
- (10) Petroleum refineries;
- (11) Lime plants;
- (12) Phosphate rock processing plants;
- (13) Coke oven batteries;
- (14) Sulfur recovery plants;
- (15) Carbon black plants (furnace process);
- (16) Primary lead smelters;
- (17) Fuel conversion plants;
- (18) Sintering plants;
- (19) Secondary metal production plants;
- (20) Chemical process plants;
- (21) Fossil-fuel boilers (or combination thereof) totaling more than 250 million British thermal units per hour heat input;
- (22) Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels;
- (23) Taconite ore processing plants;
- (24) Glass fiber processing plants;
- (25) Charcoal production plants;
- (26) Fossil fuel-fired steam electric plants of more than 250 million British thermal units per hour heat input;
- (27) Any other stationary source category which, as of August 7, 1980, is being regulated under Section 111 or 112 of the Act."

D. Emission Offset Interpretative Ruling

Appendix S of Part 51 of Title 40 of the Code of Federal Regulations is amended as follows:

1. By adding a new paragraph II.A.4(iii) to read as follows: "(iii) The fugitive emissions of a stationary source shall not be included in determining for any of the purposes of this ruling whether it is a major stationary source, unless the source belongs to one of the following categories of stationary sources:

- (a) Coal cleaning plants (with thermal dryers);
- (b) Kraft pulp mills;
- (c) Portland cement plants;
- (d) Primary zinc smelters;
- (e) Iron and steel mills;
- (f) Primary aluminum ore reduction plants;
- (g) Primary copper smelters;
- (h) Municipal incinerators capable of charging more than 250 tons of refuse per day;
- (i) Hydrofluoric, sulfuric, or nitric acid plants;
- (j) Petroleum refineries;
- (k) Lime plants;
- (l) Phosphate rock processing plants;
- (m) Coke oven batteries;
- (n) Sulfur recovery plants;
- (o) Carbon black plants (furnace process);
- (p) Primary lead smelters;
- (q) Fuel conversion plants;
- (r) Sintering plants;
- (s) Secondary metal production plants;
- (t) Chemical process plants;
- (u) Fossil-fuel boilers (or combination thereof) totaling more than 250 million British thermal units per hour heat input;
- (v) Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels;
- (w) Taconite ore processing plants;
- (x) Glass fiber processing plants;
- (y) Charcoal production plants;
- (z) Fossil fuel-fired steam electric plants of more than 250 million British thermal units per hour heat input;
- (aa) Any other stationary source category which, as of August 7, 1980, is being regulated under Section 111 or 112 of the Act."

E. Restrictions on Construction for Nonattainment Areas

Section 52.24 of Title 40 of the Code of Federal Regulations is amended as follows:

1. By adding a new paragraph (f)(4)(iii) to read as follows: "(iii) The fugitive emissions of a stationary source shall not be included in determining for any of the purposes of this section whether it is a major stationary source, unless the source belongs to one of the following categories of stationary sources:

- (a) Coal cleaning plants (with thermal dryers);
- (b) Kraft pulp mills;
- (c) Portland cement plants;
- (d) Primary zinc smelters;
- (e) Iron and steel mills;
- (f) Primary aluminum ore reduction plants;
- (g) Primary copper smelters;
- (h) Municipal incinerators capable of charging more than 250 tons of refuse per day;
- (i) Hydrofluoric, sulfuric, or nitric acid plants;
- (j) Petroleum refineries;
- (k) Lime plants;
- (l) Phosphate rock processing plants;
- (m) Coke oven batteries;
- (n) Sulfur recovery plants;
- (o) Carbon black plants (furnace process);
- (p) Primary lead smelters;
- (q) Fuel conversion plants;
- (r) Sintering plants;
- (s) Secondary metal production plants;
- (t) Chemical process plants;
- (u) Fossil-fuel boilers (or combination thereof) totaling more than 250 million British thermal units per hour heat input;
- (v) Petroleum storage and transfer units with a total storage capacity exceeding 300,000 barrels;
- (w) Taconite ore processing plants;
- (x) Glass fiber processing plants;
- (y) Charcoal production plants;
- (z) Fossil fuel-fired steam electric plants of more than 250 million British thermal units per hour heat input;
- (aa) Any other stationary source category which, as of August 7, 1980, is being regulated under Section 111 or 112 of the Act."

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ENVIRONMENTAL PROTECTION AGENCY**40 CFR Parts 51 and 52****[AD-FRL 2683-1a]****Requirements for Preparation, Adoption, and Submittal of Implementation Plans; Approval and Promulgation of Implementation Plans****AGENCY:** Environmental Protection Agency (EPA).**ACTION:** Proposal of amendments to regulations.

SUMMARY: The various EPA regulations that govern new construction under the Clean Air Act (the "Act") generally apply to "major" new stationary sources of air pollution and "major" modifications of existing sources. They require fugitive emissions to be included in threshold applicability determinations of whether a new project is "major," but only for 30 categories of sources. EPA here proposes to add surface coal mines to the current list of 30 categories and reopens the comment period on the current list. EPA is also soliciting public comment on an interpretive ruling regarding section 302(j) of the Act, 42 U.S.C. 7602(j), as it relates to the review of modifications involving fugitive emissions. In a parallel notice, EPA is announcing its reaffirmation of the current list and the legal interpretation behind it.

DATES: The period for initial comment on the addition of surface coal mines to the current list, on the list itself, and on EPA's legal interpretation of Section 302(j) with respect to modification closes on December 26, 1984. A public hearing on these items will be held in Washington, D.C., on December 3, 1984, and in Denver, Colorado, on December 7, 1984. EPA will hold the public docket for this rulemaking open for 30 days after the close of the initial comment period for the submission of written rebuttal and supplementary information.

ADDRESSES: Comments should be submitted (in triplicate, if possible) to: Central Docket Section (LE-131A), Environmental Protection Agency, 401 M Street, S.W., Washington, D.C. 20460. Attention: Docket No. A-84-33.

Public Hearing: Room 2126/2409, Waterside Mall, 401 M Street, S.W., Washington, D.C. and EPA Regional Administrator's Conference Room, 9th Floor, 1860 Lincoln Street, Denver, Colorado.

Docket: EPA has established a docket for this rulemaking, Docket No. A-84-33, in accordance with section 307(d) of the Clean Air Act, 42 U.S.C. 7607(d). The

docket is available for public inspection and copying between 8:00 a.m. and 4:00 p.m., Monday through Friday, at EPA's Central Docket Section, West Tower Lobby, Gallery I, 401 M Street, S.W., Washington, D.C. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Kirt Q. Cox, New Source Review Section, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina 27711, (919-541-5591, FTS-629-5591).

SUPPLEMENTARY INFORMATION:**I. Background**

In 1980, EPA overhauled its regulations governing the construction of new stationary sources of air pollution and modifications to existing sources in response to *Alabama Power Company v. Costle*, 636 F.2d 323 (D.C. Cir. 1979) [see 45 FR 52676 (August 7, 1980)]. The various regulations¹ that emerged from the overhaul apply generally to "major stationary sources" and "major modifications." In addition, they require "fugitive emissions"² to be included in threshold applicability determinations of whether a project is "major," but only for 30 source categories.³ Those categories do not include surface coal mines. EPA said that it would decide at a future time whether to add such mines to the list of 30 categories. The effect of this postponement was to exempt at least temporarily most surface coal mines from the substantive requirements of the relevant PSD and nonattainment regulations.

In requiring the inclusion of fugitive emissions for 30 source categories, EPA took account of section 302(j) of the Clean Air Act, 42 U.S.C. 7602(j), which provides:

Except as otherwise expressly provided, the terms "major stationary source" and

¹ One set, 40 CFR 51.24, specifies the minimum requirements that a prevention of significant deterioration (PSD) permit program must contain to warrant approval by EPA as a revision to a State implementation plan (SIP). Another set, 40 CFR 52.21, delineates the Federal PSD permit program, which currently applies in a majority of the States as part of their SIP's. Another set, 40 CFR 51.18(j), specifies the elements of an approvable state permit program for reconstruction review for nonattainment purposes. A fourth set, 40 CFR Part 51, Appendix S, embodies the "Emissions Offset Interpretive Ruling" for certain nonattainment situations. A fifth set, 40 CFR 52.24, embodies the construction moratorium for certain nonattainment areas. A sixth set, 40 CFR 51.18(k), embodies the basic requirement of section 110(a)(2)(D) that each SIP contain a permit program for "major" projects to assure they will not interfere with timely attainment and maintenance of the national ambient air quality standards (NAAQS).

² "Fugitive emissions" are emissions that would not pass through a stack or other functionally equivalent opening [e.g., 40 CFR 52.21(b)(20) (1984)].

³ See, e.g., 40 CFR 52.21 (b)(4), (i)(4)(vii) (1984).

"major emitting facility" mean any stationary facility or source of air pollutants which directly emits, or has the potential (including any major emitting facility or source of fugitive emissions of any such pollutant, as determined by rule by the Administrator).

The D.C. Circuit, in *Alabama Power*, held in light of this section that EPA may require the inclusions of fugitive emissions in threshold applicability determinations for a particular source only if it has first established through rulemaking that fugitives are to be included for that class of sources. The court did not specifically list what factors it thought EPA had to consider in such a rulemaking. EPA took the position that the section obliges it, in proposing to require inclusion for a particular category of sources, to determine at least that the sources pose a significant threat of air quality degradation and then, in taking final action, to consider, if commenters objected to the proposal, whether inclusion for the category would produce unreasonable social and economic impacts relative to the anticipated benefits. EPA added that the adequacy of methods of measuring and modeling the fugitive emissions was not by itself a decisive factor in determining whether to require inclusion, suggesting that the potential of social or economic disruption and damage to national security would have much greater weight (see generally 44 FR 52690-92).

Various industry and environmental groups, including the Sierra Club, petitioned the D.C. Circuit to review the 1980 regulations, including the provisions relating to fugitive emissions. Industry contended that EPA, in requiring the inclusion of fugitive emissions for the 30 categories, had failed to conduct the rulemaking the court had contemplated. The Sierra Club contended that EPA, in postponing a decision on strip mines, had acted arbitrarily and capriciously. The court consolidated the industry challenges under *Chemical Manufacturers Association (CMA) v. EPA*, No. 79-1112, and kept the Sierra Club challenge on its own track.

In 1982, EPA entered into a settlement agreement with the industry petitioners in the *CMA* case. EPA committed to propose, among other things, to delete the requirement for including fugitive emissions for the 30 categories and to take final action on the proposal. The court stayed the litigation pending implementation of the agreement.

On August 25, 1983, 48 FR 38742, EPA proposed to delete that requirement. EPA stated that it had concluded preliminarily that its original

interpretation of section 302(j) was wrong.

In a *Federal Register* notice that parallels this one, EPA is announcing a final action on that proposal which reaffirms the current requirements. EPA states that it has concluded that its original interpretation was correct after all. Thus, EPA continues to view section 302(j) as requiring it to determine only that (1) the sources in a category could degrade air quality significantly, and (2) no factors raised by commenters during the comment period indicate that listing the category would produce unreasonable social and economic impacts when compared to the benefits of listing. In performing rulemaking for a particular source category, the Agency regards the first determination as establishing a presumption in favor of listing the category that could be rebutted only by an analysis which proves that unreasonable costs would result taking into account all positive aspects of the listing. The reader should see the companion notice for a more detailed explanation of this "safety valve" interpretation of Section 302(j) and the reaffirmation of the current listing.

Meanwhile, on August 26, 1983, in the *Sierra Club* case, the D.C. Circuit remanded EPA's postponement of action on strip mines, ruling that EPA under the logic of its 1980 action appeared to have no good reason for listing the 30 categories but not strip mines (715 F. 2d 653). In EPA's response to the remand, it agreed with that ruling and committed to propose to list or not list strip mines. The court then ordered EPA to propose one way or the other by October 22, 1984.

II. Proposal to List Surface Coal Mines

EPA has concluded on the basis of various studies⁴ that surface coal mines do pose a threat of significant air quality degradation. Most such mines of an economically viable size emit in excess of 250 tons per year, the volume of emissions that Congress found significant in section 169(1) of the Act, 42 U.S.C. 7479(1), for sources outside the 28 categories listed in that section. EPA therefore proposed to add surface coal mines to the current list of 30 categories of sources whose fugitive emissions are to be included in threshold applicability determinations. EPA solicits comments on this proposal.⁵

EPA fully expects that weighty objections to the listing of surface coal mines will be raised. EPA expects these to include claims that such mines simply cannot meet PSD requirements if they are listed, and that to prevent the opening of new surface mines by subjecting them to PSD requirements would not serve either the cause of a sound energy policy or the broader national interest. Moreover, surface mines differ from many other sources of pollution in that they must be located where the mineral deposit on which they depend is found, and therefore have limited geographical mobility.

The fact that EPA is proposing to list surface coal mines does not mean that it has determined that these factors lack merit, or that it is in some way unlikely to give weight to them at the time of final promulgation. Rather, as today's companion notice makes clear, EPA believes that the "safety valve" function of section 302(j) is best served if these broader issues are first raised in public comments and thereafter considered by EPA in making its final decision.

Because of particular concern with longstanding problems arising from the regulation of surface mining and the requirements of Executive Order 12291, EPA is independently preparing an analysis of the effects of adding strip mines to the current list.⁶ EPA intends to make the results of the study available to the public for comment before the Agency takes final action on today's proposal.

EPA is analyzing the nature of the surface coal mining industry and is assembling information regarding the size, number, location, and lifespan of mines, and the rate, size and location of industry growth. After addressing the population of mines that could be subject to PSD permitting requirements, an analysis will be prepared of the costs of PSD review to them. This includes the

statement agreement in *EDF v. EPA*, N.D. Calif. No. C82-6850 RPA. EPA anticipates that such SIP's will contain similar lists of source categories whose fugitive emissions would be included in threshold applicability determinations. EPA also proposed to add surface coal mines to those lists if and when these are promulgated. EPA solicits comment on such an action at this time.

⁴As EPA stated in the companion notice, it does not view section 302(j) as barring the preparation of a cost/benefit analysis prior to a proposal or final action under the section, but rather as allowing EPA not to prepare one. Under normal circumstances, EPA would have prepared such an analysis under E.O. 12291 for the strip mines proposal here. EPA is constrained by the court ordered deadline of October 22, 1984, to propose action on strip mines without having completed such an analysis. Nevertheless, that analysis will be completed prior to final action. Moreover, for future proposals as to other source categories, if any, EPA intends to adhere to the applicable requirements for cost benefit analysis under the Executive Order.

cost of preparing a permit application and of applying best available control technology to mine operations. Most significantly, the study is addressing the costs that would accrue to the mining industry as a result of the constraints from the PSD increments. Analysis is also being prepared on the degree of emissions reductions that the increments and NAAQS might require and the estimated benefits to public health and welfare that would arise from it.

This study will also address potential impact on Class I areas. Protection of Class I areas, such as national parks, has long been a special concern and may present a rationale for regulation of mines which would affect them that is considerably stronger than it is for mines locating in order areas. EPA therefore solicits comments on the possibility of restricting the applicability of the relevant regulations to those surface coal mines that would affect Class I areas and possibly the mandatory Class II areas⁷ as well. One issue is whether section 302(j) provides authority to list only a subclass of surface coal mines. EPA is inclined to conclude that it does. Another issue is whether the balance of benefits and costs to society justify a distinction along those lines.

In addition, EPA also solicits comment on whether the existing strip mines that the proposed listing would render "major" should consume PSD increment. Section 169(4) of the Act provides that all major emitting facilities on which construction commenced after January 6, 1975, are not to be included in the baseline concentration and instead consume the available PSD increment. A listing of surface coal mines pursuant to section 302(j) would cause many of them to be classified as major sources. This raises the issue whether section 169(4) would require all large mines that commenced construction (even though not then as "major" stationary sources) since January 6, 1975, but prior to today, to retroactively consume increment instead of continuing to contribute to baseline concentration. EPA does not believe that the Congress intended such a disruption to occur. Instead, the Agency believes that it should "grandfather" existing mines from retroactive consumption of increment but seeks public comment on this matter. The effects of not doing so will be addressed to a limited degree in EPA's study.

⁷Such areas are described in section 164(a) of the Act, 42 U.S.C. 7474(a).

⁴Characterization of PM₁₀ and TSP Air Quality Around Western Surface Coal Mines, PEDCo Environmental, Inc., and TRC Environmental Consultants [EPA Contract No. 68-02-3512 (August 1982)].

⁵EPA is obligated to propose visibility new source review SIP's for numerous States under a

Any grandfathering from increment consumption granted must be reasonably bounded. The Agency proposes that this exemption be granted to all mines which have commenced construction prior to the date of final action on this notice. "Commencement of construction" is the key term. For the purposes of this action, EPA suggests that the term includes the receipt of all necessary permits plus certain other activities evidencing a commitment to the project. These may include on-site activity or site specific contracts. Because of the location specific nature of mining permits and possibility that factors other than those applicable to a conventional industrial source may be germane, EPA solicits comment on an appropriate policy for addressing the potential grandfathering of mines within the presently applicable definitions of commencement of construction. EPA also proposes to extend an exemption from PSD permitting requirements to these same sources. Today's notice contains proposed regulations to accomplish both of these grandfathering actions. Public comment is also solicited on these proposed regulations.

III. Reopening of Comment Period on the List of Thirty Categories

As explained in detail in the companion notice, although EPA has reaffirmed the list of 30 source categories and the underlying statutory interpretation, it recognizes it could have provided a fuller opportunity to comment on the original listing. Therefore, as a policy matter, EPA is reopening the comment period for the current list of 30 categories, and solicits comments on that list.

Consistent with its "safety valve" interpretation of Section 302(j), however, EPA is inclined not to remove a category from the list unless a commenter shows adverse consequences to the board national interest in continuing the listing.

IV. Nonapplicability of Section 302(j) to Modifications

In overhauling its new source review regulations in 1980 and in proposing further amendments in 1983, EPA assumed that the rulemaking requirement in section 302(j) applies to modifications as well as to sources. The litigants and commenters have all carried that assumption into their communications, without evidencing any examination of it. Drawn by the latest round of proposal and comment into examining the assumption, EPA has concluded that it appears to be incorrect. This section of this notice outlines the reasons for that conclusion

and solicits comment on it. After evaluating any comments, EPA may translate the conclusion directly without further comment into regulatory amendments.*

The literal language of the Act strongly suggests that Congress did not intend the rulemaking requirement in section 302(j) to apply to modifications. First, section 302(j) on its face applies only to new and existing emissions units and, hence, not to modifications. It provides that:

the terms "major stationary source" and "major emitting facility" mean any *stationary facility or source* [that has a certain pollution potential] (including any major emitting facility or source of fugitive emission * * * as determined by rule by the Administrator). [42 U.S.C. 7602(j) (emphasis added)].

Plainly, this language explicitly attached the rulemaking requirement only to proposed or actual units; it says nothing about modifications to such units.

In contrast, Parts C and D, the provisions that detail the applicability and content of the PSD and nonattainment new source review program, expressly define the term "modification" by reference to a parallel definition which appears to require the inclusion of fugitive emissions in threshold applicability determinations for modifications. Section 169(2)(C), 42 U.S.C. 7479(2)(C), states, for purposes of Part C, that:

[t]he term "construction" when used in connection with any source or facility, includes the modification *(as defined in section 111(a) of this title)* of any source or facility. [Emphasis added.]

Similarly, section 171(4), 42 U.S.C. 7501(4), provides, for purposes of both Part D and the construction ban in section 100(a)(2)(I), that:

[t]he terms "modification" and "modified" mean the same as the term "modification" *as used in section 111(a)(4) of this title*. [Emphasis added.]

Section 111(a)(4), 42 U.S.C. 7411(a)(4), in turn provides that:

[t]he term "modification" means any physical change in, or change in the method of operation of, a stationary source *which increases the amount of any air pollutant emitted by such source or which results in the emissions of any air pollutant not previously emitted*. [Emphasis added.]

*Specifically, EPA would not promulgate the amendment to the definition of "major modification" that was proposed on August 25, 1983, namely those proposed as §§ 51.24(b)(2)(iv), 52.21(b)(2)(iv), 51.18(j)(1)(v)(d), IIA.5(iv) of Appendix S to Part 51, and 52.24(f)(5)(iv). EPA would also add a provision to the relevant regulations that would "grandfather" any modifications that (1) would not have been subject to review but for the deletion of those amendments and (2) commenced construction before the final deletion.

In defining "modification" solely in terms of the total amount of pollution that a source change would produce, section 111(a)(4) suggests that Congress intended to establish here no qualitative distinction between emissions, and, hence, to require the inclusion of fugitive emissions for modifications, without any intermediate rulemaking step.

The legislative history strongly supports this view that Congress intended the section 302(j) rulemaking requirement not to apply to modifications. First, the passages in the relevant House and conference reports that focus on section 302(j) refer, as does section 302(j), only to proposed and existing emissions units, and not at all to modifications [see H.R. Report No. 95-294, 95th Cong., 1st Sess. 4, 9, 144 (1977); H.S. Rep. No. 95-564, 95th Cong., 1st Sess. 172 (1977)]. In addition, the explanation by the conference committee of section 169(2)(C) states that it:

[i]mplements conference agreement to cover "modification" as well as "construction" by defining "construction" in Part C *to conform to usage in other parts of the Act*. [123 Cong. Rec. H 11957, col. 3 (daily ed.) (November 1, 1977) (emphasis added).]

The phrase "usage in other parts of the Act" most probably refers, not only to section 111(a)(4), but also to the EPA regulations implementing section 111 that were in effect at the time. Like section 111(a)(4), those regulations on their face require the inclusion of fugitive emissions in section 111 applicability determination, inasmuch as they concern themselves only with the quantity of the emissions in question [see 40 CFR 60.14(a) (1977)]. Finally, EPA and the States prior to enactment of section 302(j) in 1977 made no distinction between fugitive and nonfugitive emissions in threshold applicability determinations [see, e.g., 40 CFR 51.18 (1977); 41 FR 55528 (December 21, 1976) (the original Offset Ruling), 40 CFR 51.21(d)(1) (1977) (original PSD regulations)]. Section 302(j), therefore, ran against the grain of longstanding practice. If Congress had intended a change as to modifications, it probably would have said so explicitly, yet it said nothing.

EPA's new interpretation as to the applicability of the section 302(j) rulemaking requirement is consistent with Congress' purposes. Requiring fugitive emissions to be included in threshold applicability determinations for modifications would not frustrate the protections from the burdens of new source review that the rulemaking requirement affords. Under the Act and EPA regulations, a modification is

"major" and subject to review only if the source at which it would occur is also "major" [see, e.g., 40 CFR 52.21(b)(2)(i) (1984)]. Hence, a modification to a source of predominantly fugitive emissions that does not belong to a currently listed category, for instance a surface coal mine, could not be subject to review, even if its fugitive emissions were taken into account, because the source would not be "major". In addition, requiring fugitive emissions to be included in threshold applicability determinations would promote the Congressional goal of minimizing unnecessary burdens. As discussed at length in the preamble to the 1983 proposal and in the comments (see, e.g., 48 FR 38746), the exclusion of fugitive emissions decreases, as well as increases, in threshold applicability determinations for modifications can result in a company having to obtain a permit, but not having to meet any substantive requirements to obtain it. The universal inclusion of fugitive emissions increases and decreases would cure this problem of an empty proceeding. Finally, universal inclusion removes any incentive a company would otherwise have to artificially sequence the construction of a group of modifications so that the modifications that produce only fugitive emissions might escape review on the theory that they are separate and not "major."

V. Miscellaneous

A. Docket

EPA has established a docket for this rulemaking, Docket No. A-84-33. The docket is an organized and complete file of all significant information submitted to or otherwise considered by EPA during this proceeding. The contents of the docket will serve as the record in the case of judicial review under section 307(b) of the Act, 42 U.S.C. 7607(b). The docket is available for public inspection and copying between 8:00 a.m. and 4:00 p.m., Monday through Friday, at EPA's Central Docket Section, West Tower Lobby, Gallery I, 401 M Street, S.W., Washington, D.C. A reasonable fee may be charged for copying.

B. Public Hearing

EPA will hold a public hearing on December 4, 1984, at 10:00 a.m., in Room 2126/2409, Waterside Mall, 401 M Street, S.W., Washington, D.C., and on December 6, 1984, at 10:00 a.m., in EPA Regional Administrator's Conference Room, 9th Floor, 1860 Lincoln Street, Denver, Colorado. The hearings will be informal. A panel of EPA staff will hear the oral presentations. There will be no cross-examination and no requirement

that any person be under oath. Each member of the panel may seek clarification or amplification of any presentation. The presiding officer of the panel may set a time limit for each presentation and may restrict any presentation that would be irrelevant or repetitious. A transcript of each hearing will be made and placed in the rulemaking docket.

Any person who wishes to speak at a hearing should as soon as possible send written notice of this to EPA, give name, address, telephone number, and the length of the presentation. Anyone stating that his or her presentation would be longer than 20 minutes should also state why it need be longer. Each notice should be sent to Kirt Q. Cox, at the address given at the beginning of this notice. EPA will develop a schedule for presentations based on the notices it receives. Anyone who fails to submit a notice, but wishes nevertheless to speak at the hearing should so notify the presiding officer immediately before the hearing. The presiding officer will decide whether, when, and for how long the person may speak. Each speaker should bring extra copies of his or her presentation for the convenience of the hearing panel, the hearing reporter, the press, and other participants. The hearings will be open to the public.

C. Executive Order 12291

Under Executive Order 12291, EPA must prepare a regulatory impact analysis for any regulation that qualifies as a "major rule." A major rule is defined as any regulation that is likely to result in an annual effect on the economy of \$100 million or more. EPA has determined that the proposal to list strip mines might have an annual effect on the economy of \$100 million or more, and EPA is therefore preparing the economic analysis described above in section II. EPA has determined, on the other hand, that the proposed new interpretation of section 302(j) as it relates to modifications will not have sufficient economic effect to be considered a major rule. The new interpretation will not require large numbers of additional modifications to obtain permits because there are relatively few modifications involving fugitive emissions at major sources other than those sources already on the current list of 30 source categories. Those modifications must presently obtain permits under the existing regulations; therefore, EPA is not preparing a regulatory impact analysis for this portion of the rulemaking.

These regulations have been submitted to the Office of Management and Budget for review under Executive

Order 12291. Any comments from the office, and EPA's responses to any such comments, will be placed in the docket for this proceeding and are available for public inspection at the times and place described earlier in this preamble.

D. Economic Impact Assessment

Section 317 of the Clean Air Act, 42 U.S.C. 7617, requires EPA to prepare an economic impact assessment in connection with proposal of any substantial revisions to existing regulations. The economic analysis concerning strip mines that EPA is preparing in order to comply with Executive Order 12291 will also satisfy the requirement for preparation of an economic impact assessment on the proposal to list strip mines. This analysis will be available to the public within the next few months. The comment period on these proposed regulations will be provided to allow the public sufficient time to comment on the analysis. EPA will not be preparing an economic analysis on the new interpretation of section 302(j) as it relates to modifications because this is not a substantial revision. As discussed above, this interpretation will not bring many additional modifications under review.

E. Regulatory Flexibility Act Certification

As required by section 3(a) of the Regulatory Flexibility Act, 5 U.S.C. 605(b), I certify that this regulation will not have a significant adverse impact on a substantial number of small entities. The proposal to list strip mines will primarily effect large mining operations. The proposed new interpretation of section 302(j) as it relates to modifications will not bring a large number of additional modifications into the permitting system.

F. Paperwork Reduction Act

The Office of Management and Budget (OMB) has approved some of the information collection requirements contained in this proposed rule under the provisions of the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.* and has assigned OMB control number 2060-0003. This proposed rule also introduces additional requirements, and these have been transmitted to OMB. Comments on these requirements should be submitted to the office of Information and Regulatory Affairs of OMB, marked "Attention: Desk Officer for EPA." The final rule will respond to any OMB or public comments on the information collection requirements.

List of Subjects

40 CFR Part 51

Administrative practice and procedures, Air pollution control, Intergovernmental relations, Reporting and recordkeeping requirements, Ozone, Sulfur Oxides, Nitrogen dioxide, Lead, particulate matter, Hydrocarbon, Carbon monoxide.

40 CFR Part 52

Air pollution control, Ozone, Sulfur oxides, Nitrogen dioxide, Lead, Particulate matter, Carbon monoxide, Hydrocarbons.

Authority: Sections 101(b)(1), 160-169, 171-178, and 301(a) of the Clean Air Act as amended [42 U.S.C. 7401(b)(1), 7410, 7470-79, 7501-08 and 7601(a)]; Section 129(a) of the Clean Air Act Amendments of 1977 [Pub. L. No. 95-95, 91 Stat. 685 (August 7, 1977)].

Dated: October 19, 1984.

Alvin L. Alm,

Deputy Administrator.

Title 40 of the Code of Federal Regulations, as amended, is proposed to be amended, as follows:

PARTS 51 AND 52—[AMENDED]

A. Requirements for State PSD Plans

§ 51.24 [Amended]

Section 51.24 of Title 40 of the Code of Federal Regulations is proposed to be amended as follows:

1. By redesignating paragraph (aa) of § 51.24(b)(1)(iii), as (bb) to and adding a new paragraph (aa) to read as follows: "(aa) Surface coal mines,";

2. By adding a new paragraph (b)(13)(iii) to read as follows: "(iii) The actual emissions of coal surface mines on which construction commenced prior to [the date that final action for the listing of surface coal mines is published in the Federal Register] will not affect the applicable maximum allowable increase, unless such emissions occurred after an applicable baseline date has been established for the affected area.";

3. By adding a new paragraph (i)(4)(iv) to read as follows: "(iv) The source or modification is a surface coal mine otherwise qualifying as a new or modified major stationary source under this section if the owner or operator:

(a) Obtained all final federal, state, and local preconstruction approvals or permits necessary under the applicable State implementation plan before [the date that final action for the listing of surface coal mines is published in the Federal Register];

(b) Commenced construction within 18 months from [the date that final action for the listing of surface coal mines is

published in the Federal Register], or any earlier time required under the State implementation plan; and

(c) Did not discontinue construction for a period of 18 months or more and completed construction within a reasonable time."

B. New Source Review for PSD Purposes

§ 52.21 [Amended]

Section 52.21 of Title 40 of the Code of Federal Regulations is proposed to be amended as follows:

1. By redesignating paragraph (aa) of § 52.21(b)(1)(iii), as (bb) and adding a new paragraph (aa) to read as follows: "(aa) Surface coal mines,";

2. By adding a new paragraph (b)(13)(iii) to read as follows: "(iii) The actual emissions of coal surface mines on which construction commenced prior to [the date that final action for the listing of surface coal mines is published in the Federal Register] will not affect the applicable maximum allowable increase, unless such emissions occurred after an applicable baseline date has been established for the affected area.";

3. By adding a new paragraph (i)(4)(ix) to read as follows: "(ix) The source or modification is a surface coal mine otherwise qualifying as a new or modified major stationary source under this section if the owner or operator:

(a) Obtained all final federal, state, and local preconstruction approvals or permits necessary under the applicable State implementation plan before [the date that final action for the listing of surface coal mines is published in the Federal Register];

(b) Commenced construction within 18 months from [the date that final action for the listing of surface coal mines is published in the Federal Register], or any earlier time required under the State implementation plan; and

(c) Did not discontinue construction for a period of 18 months or more and completed construction within a reasonable time.

C. State Plans for New Source Review for Nonattainment Purposes

§ 51.18 [Amended]

Section 51.18 of Title 40 of the Code of Federal Regulations is proposed to be amended as follows:

1. By redesignating paragraph "(27) of § 51.18(j)(1)(iv)(c) as (28) and adding a new paragraph (27) to read as follows: "(27) Surface Coal Mines"; and

2. By adding a new paragraph (j)(6) to read as follows: "(6) Each plan may provide that the requirements of this subsection do not apply to the

construction of a surface coal mine otherwise qualifying as a new or modified major stationary source under this section if the owner or operator:

(i) Obtained all final federal, state, and local preconstruction approvals or permits necessary under the applicable State implementation plan before [the date that final action for the listing of surface coal mines is published in the Federal Register];

(ii) Commenced construction within 18 months from [the date that final action for the listing of surface coal mines is published in the Federal Register], or any earlier time required under the State implementation plan; and

(iii) Did not discontinue construction for a period of 18 months or more and completed construction within a reasonable time.

D. Emission Offset Interpretative Ruling

Appendix S [Amended]

Appendix S of Part 51 of Title 40 of the Code of Federal Regulations is proposed to be amended as follows:

1. By redesignating paragraph (aa) of II.A.4(iii) as (bb) and adding a new paragraph (aa) to read as follows: "(aa) Surface Coal Mines,";

2. By adding a new paragraph II.E. to read as follows: "II.E. Section IV.A. of this Ruling shall not apply to the construction of a coal surface mine otherwise qualifying as a new or modified major stationary source under this section if the owner or operator:

(a) Obtained all final federal, state, and local preconstruction approvals or permits necessary under the applicable State implementation plan before [the date that final action for the listing of surface coal mines is published in the Federal Register];

(b) Commenced construction within 18 months from [the date that final action for the listing of surface coal mines is published in the Federal Register], or any earlier time required under the State implementation plan; and

(c) Did not discontinue construction for a period of 18 months or more and completed construction within a reasonable time.

E. Restrictions on Construction for Nonattainment Areas

§ 52.24 [Amended]

Section 52.24 of Title 40 of the Code of Federal Regulations is proposed to be amended as follows:

1. By redesignating paragraph (aa) of § 52.24(f)(4)(iii) as (bb) and adding a new paragraph (aa) to read as follows: "(aa) Surface Coal Mines,";

2. By adding a new paragraph (e) to read as follows: "(e) This section shall not apply to the construction of a surface coal mine otherwise qualifying as a new or modified major stationary source under this section if the owner or operator:

(1) Obtained all final federal, state, and local preconstruction approvals or

permits necessary under the applicable State implementation plan before [the date that final action for the listing of surface coal mines is published in the Federal Register];

(2) Commenced construction within 18 months from [the date that final action for the listing of surface coal mines is published in the Federal Register], or

any earlier time required under the State implementation plan; and

(3) Did not discontinue construction for a period of 18 months or more and completed construction within a reasonable time.

[FR Doc. 84-28200 Filed 10-25-84; 8:45 am]

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Federal Register

Friday
October 26, 1984

Part VI

Department of Transportation

Urban Mass Transportation
Administration

Fiscal Year 1985 UMTA Formula Grant
Apportionments; Notice

DEPARTMENT OF TRANSPORTATION**Urban Mass Transportation
Administration****Fiscal Year 1985 UMTA Formula Grant
Apportionments****AGENCY:** Urban Mass Transportation
Administration (UMTA), DOT.**ACTION:** Notice.

SUMMARY: The Federal Public Transportation Act of 1982 (Pub. L. 97-424) established a formula grant program for Fiscal Years 1984, 1985 and 1986 under Section 9 and Section 18 of The Urban Mass Transportation Act of 1964, as amended. This Notice provides the Fiscal Year 1985 apportionment of funds to each urbanized area over 200,000 in population, and to State Governors for apportionment to urbanized areas under 200,000 in population and to rural areas.

FOR FURTHER INFORMATION CONTACT: Edward R. Fleischman, Chief, Resource Management Division, (202) 426-2053, 400 Seventh Street, SW., Washington, DC. 20590.

SUPPLEMENTARY INFORMATION: A program of federal assistance to urban mass transportation systems by means of formula grants for capital and operating assistance was enacted January 6, 1983, under the Federal Public Transportation Act of 1982 (Pub. L. 97-424). The legislation is authorized for Fiscal Years 1984, 1985, and 1986. Funds for Fiscal Year 1985 were appropriated by Pub. L. 98-473.

This Notice, based on Census information and operating and financial data contained in the section 15 Report, provides the Fiscal Year 1985 apportionment of section 9 and section 18 funds for urbanized and nonurbanized areas. Applications for section 9 funds should be submitted in conformance with UMTA Circular 9030.1, published June 27, 1983.

Applications for section 18 funds should be submitted in conformance with UMTA Circular 9040.1, published September 26, 1983.

The funds shown in this Notice apportioned to urbanized areas will remain available to be obligated by UMTA to recipients for three (3) fiscal years following Fiscal Year 1985, after which time any unobligated funds will become available for reapportionment under section 9. Funds apportioned to nonurbanized areas will remain available to be obligated by UMTA to recipients for two (2) years following Fiscal Year 1985, after which time any unobligated funds will become available for reapportionment under section 18.

Corrections have been made to the data from certain urbanized areas that were used to compute the Fiscal Year 1984 formula grant apportionments published in the *Federal Register* of November 2, 1983 (48 FR 50656). Differences between corrected apportionments and previously published apportionments have been determined, and necessary adjustments have been made by adding to or subtracting from, as appropriate, the apportionments calculated for Fiscal Year 1985.

For urbanized areas over 200,000 in population, funds apportioned under section 9 are based, in part, on data collected through the section 15 reporting system. In the process of collecting these data, there have been repeated problems with late reports, missing certifications and the inclusion of possible erroneous data in vehicle revenue miles (see UMTA Circular 9030.1 for definitions). The issues are summarized below:

Late reports. UMTA regulations require transit agencies to submit section 15 reports within 120 calendar days of the end of their fiscal year. Many agencies have been delinquent in submitting their section 15 report or

have submitted incomplete reports. This makes it difficult for UMTA to validate the data and increases the risk of erroneous data being used in the apportionment.

Independent certification. All reporters in urbanized areas of 200,000 or more are required to submit with their section 15 reports a certification by an independent auditor of the recordkeeping system and definitions used to collect data used in the Section 9 apportionment formula. When reporters fail to comply with this requirement, it calls into question the validity of the data submitted.

Deadhead mileage. Certain agencies have not made the appropriate adjustment between total vehicle mileage and vehicle revenue mileage as required. The difference between these two figures represents deadhead mileage, which is not included in the data used for the apportionment. Those urbanized areas that include deadhead mileage in the vehicle revenue mileage reported receive a greater apportionment than they are entitled to while reducing the apportionments of those reporters who follow the definition of revenue vehicle mileage.

These issues have resulted in problems in the timeliness of UMTA's publication of apportionment data, and in some cases raise questions about the validity of certain submitted data. In this connection, UMTA is planning to issue a notice of proposed rulemaking that would propose penalties to address this problem. These penalties could affect an area's ability to receive apportioned funds for failure to report in a timely manner, provide certifications, or submit data which are in accordance with UMTA definitions.

Issued on: October 17, 1984.

Ralph L. Stanley,
Administrator.

BILLING CODE 84-28322-M

**FISCAL YEAR 1985 UMTA SECTION 9 FORMULA APPORTIONMENTS
AMOUNTS APPORTIONED TO URBANIZED AREAS OVER 200,000 POPULATION**

URBANIZED AREA	APPORTIONMENT	URBANIZED AREA	APPORTIONMENT
Akron, Ohio	\$ 4,929,697	Madison, Wisconsin	\$ 4,346,370
Albany-Schenectady-Troy, New York	8,374,270	Melbourne-Cocoa, Florida	1,128,920
Albuquerque, New Mexico	4,312,685	Memphis, Tennessee-Arkansas-Mississippi	7,829,691
Allentown-Bethlehem-Easton, Pa.-N.J.	3,537,492	Miami, Florida	22,087,236
Ann Arbor, Michigan	2,323,863	Milwaukee, Wisconsin	17,224,234
Atlanta, Georgia	25,488,902	Minneapolis-St. Paul, Minnesota	19,784,348
Augusta, Georgia-South Carolina	1,613,077	Mobile, Alabama	1,901,700
Austin, Texas	3,827,942	Nashville-Davidson, Tennessee	4,608,676
Bakersfield, California	2,247,405	New Haven, Connecticut	6,440,623
Baltimore, Maryland	27,077,092	New Orleans, Louisiana	14,990,274
Baton Rouge, Louisiana	2,919,220	Newport News-Hampton, Virginia	3,164,708
Birmingham, Alabama	4,533,656	New York, N.Y.-Northeastern New Jersey	605,064,321
Boston, Massachusetts	67,359,107	Norfolk-Portsmouth, Virginia	8,879,475
Bridgeport, Connecticut	5,642,655	Ogden, Utah	2,536,128
Buffalo, New York	10,658,219	Oklahoma City, Oklahoma	4,148,307
Canton, Ohio	1,917,281	Omaha, Nebraska-Iowa	6,274,493
Charleston, South Carolina	1,349,742	Orlando, Florida	4,271,798
Charlotte, North Carolina	3,403,943	Oxnard-Ventura-Thousand Oaks, California	3,692,403
Chattanooga, Tennessee-Georgia	2,225,477	Pensacola, Florida	1,391,021
Chicago, Illinois-Northwestern Indiana	181,648,252	Peoria, Illinois	2,285,278
Cincinnati, Ohio-Kentucky	12,524,229	Philadelphia, Pennsylvania-New Jersey	108,609,372
Cleveland, Ohio	25,322,268	Phoenix, Arizona	11,356,875
Colorado Springs, Colorado	2,510,731	Pittsburgh, Pennsylvania	33,979,415
Columbia, South Carolina	1,361,130	Portland, Oregon-Washington	17,405,100
Columbus, Georgia-Alabama	1,846,178	Providence-Pawtucket-Warwick, R.I.-Mass.	13,875,854
Columbus, Ohio	10,713,064	Raleigh, North Carolina	1,871,219
Corpus Christi, Texas	1,846,770	Richmond, Virginia	5,557,753
Dallas-Fort Worth, Texas	21,231,745	Rochester, New York	7,323,171
Davenport-Rock Island-Moline, Iowa-Illinois	2,662,927	Rockford, Illinois	1,995,552
Dayton, Ohio	12,563,622	Sacramento, California	8,995,978
Denver, Colorado	16,865,486	St. Louis, Missouri-Illinois	19,985,924
Des Moines, Iowa	2,615,319	St. Petersburg, Florida	7,537,603
Detroit, Michigan	46,240,969	Salt Lake City, Utah	8,889,233
El Paso, Texas	5,691,747	San Antonio, Texas	13,749,546
Fayetteville, North Carolina	1,257,625	San Bernardino-Riverside, California	7,792,108
Flint, Michigan	2,796,941	San Diego, California	28,129,504
Fort Lauderdale-Hollywood, Florida	9,082,408	San Francisco-Oakland, California	103,691,323
Fort Wayne, Indiana	2,331,787	San Jose, California	20,909,604
Fresno, California	3,796,942	San Juan, Puerto Rico	15,507,178
Grand Rapids, Michigan	3,794,004	Sarasota-Bradenton, Florida	2,450,187
Greenville, South Carolina	1,255,915	Scranton-Wilkes-Barre, Pennsylvania	3,708,253
Harrisburg, Pennsylvania	2,732,046	Seattle-Everett, Washington	34,531,593
Hartford, Connecticut	7,449,961	Shreveport, Louisiana	2,553,883
Honolulu, Hawaii	18,311,649	South Bend, Indiana-Michigan	2,366,123
Houston, Texas	27,272,483	Spokane, Washington	4,334,020
Indianapolis, Indiana	8,029,277	Springfield-Chicopee-Holyoke, Mass.-Conn.	5,305,326
Jackson, Mississippi	1,727,578	Syracuse, New York	5,231,074
Jacksonville, Florida	5,969,070	Tacoma, Washington	6,002,007
Kansas City, Missouri-Kansas	8,523,728	Tampa, Florida	5,540,712
Knoxville, Tennessee	2,743,631	Toledo, Ohio-Michigan	6,501,565
Lansing, Michigan	2,631,203	Trenton, New Jersey-Pennsylvania	6,854,298
Las Vegas, Nevada	3,164,311	Tucson, Arizona	5,647,661
Lawrence-Haverhill, Mass.-New Hampshire	2,765,605	Tulsa, Oklahoma	3,730,245
Little Rock-North Little Rock, Arkansas	2,406,903	Washington, D.C.-Maryland-Virginia	68,252,428
Lorain-Elyria, Ohio	994,410	West Palm Beach, Florida	3,826,276
Los Angeles-Long Beach, California	142,139,674	Wichita, Kansas	2,739,869
Louisville, Kentucky-Indiana	9,456,354	Wilmington, Delaware-New Jersey-Maryland	4,147,679
		Worcester, Massachusetts	2,795,342
		Youngstown-Warren, Ohio	2,574,154

**FISCAL YEAR 1985 UMTA SECTION 9 FORMULA APPORTIONMENTS
AMOUNTS APPORTIONED TO AREAS UNDER 200,000 POPULATION**

STATE/URBANIZED AREA	APPORTIONMENT	STATE/URBANIZED AREA	APPORTIONMENT
ALABAMA:		COLORADO:	
Governor's apportionment for areas 50,000 to 200,000 population	\$ 5,779,318	Governor's apportionment for areas 50,000 to 200,000 population ..	\$ 3,820,739
Anniston	501,775	Boulder	947,106
Auburn-Opelika	311,952	Fort Collins	703,674
Decatur	365,425	Grand Junction	457,107
Dothan	320,267	Greeley	672,717
Florence	490,772	Pueblo	1,040,135
Gadsden	462,476		
Huntsville	1,031,991	Non-urbanized	703,095
Montgomery	1,539,604		
Tuscaloosa	755,056		
Non-urbanized	1,714,383		
ALASKA:		CONNECTICUT:	
Governor's apportionment for areas 50,000 to 200,000 population	1,171,880	Governor's apportionment for areas 50,000 to 200,000 population	16,187,091
Anchorage	1,171,880	Bristol	666,121
Non-urbanized	186,550	Danbury, Conn.-N.Y.	2,602,453
		Meriden	542,368
ARIZONA:		New Britain	1,340,061
Governor's apportionment for areas 50,000 to 200,000 population	504,708	New London-Norwich	1,099,013
Yuma, Ariz.-Calif.	504,708	Norwalk	2,909,631
Non-urbanized	648,105	Stamford	3,627,840
		Waterbury	3,399,604
ARKANSAS:		Non-urbanized	638,541
Governor's apportionment for areas 50,000 to 200,000 population	1,702,972		
Fayetteville-Springdale	405,109	DELAWARE:	
Fort Smith, Ark.-Okla.	605,737	Non-urbanized	182,661
Pine Bluff	555,429		
Texarkana, Tex.-Ark.	136,697		
Non-urbanized	1,387,894		
CALIFORNIA:		FLORIDA:	
Governor's apportionment for areas 50,000 to 200,000 population	17,287,920	Governor's apportionment for areas 50,000 to 200,000 population	7,987,616
Antioch-Pittsburg	970,617	Daytona Beach	1,319,668
Chico	449,498	Fort Myers	1,048,156
Fairfield	612,068	Fort Pierce	494,377
Hemet	468,180	Fort Walton Beach	619,468
Lancaster	391,909	Gainesville	881,149
Modesto	1,838,887	Lakeland	850,610
Napa	640,717	Naples	353,753
Palm Springs	435,084	Ocala	352,607
Redding	359,436	Panama City	566,425
Salinas	1,188,955	Tallahassee	947,939
Santa Barbara	1,690,384	Winter Haven	553,464
Santa Cruz	962,285	Non-urbanized	1,866,939
Santa Maria	544,206		
Santa Rosa	1,344,011	GEORGIA:	
Seaside-Monterey	1,247,299	Governor's apportionment for areas 50,000 to 200,000 population	4,448,850
Simi Valley	837,491	Albany	641,762
Stockton	2,196,533	Athens	474,175
Visalia	544,636	Macon	1,142,323
Yuba City	563,490	Rome	361,518
Yuma, Ariz.-Calif.	2,234	Savannah	1,381,376
Non-urbanized	3,138,108	Warner Robins	447,696
		Non-urbanized	2,303,529
		HAWAII:	
		Governor's apportionment for areas 50,000 to 200,000 population	1,140,229
		Kailua-Kaneohe	1,140,229
		Non-urbanized	222,725

**FISCAL YEAR 1985 UMTA SECTION 9 AND SECTION 18 FORMULA APPORTIONMENTS
AMOUNTS APPORTIONED TO AREAS UNDER 200,000 POPULATION—(Continued)**

STATE/URBANIZED AREA	APPORTIONMENT	STATE/URBANIZED AREA	APPORTIONMENT
IDAHO:		KENTUCKY:	
<i>Governor's apportionment for areas</i>		<i>Governor's apportionment for areas</i>	
50,000 to 200,000 population	\$ 1,654,671	50,000 to 200,000 population	\$ 3,429,414
Boise City	1,194,830	Clarksville, Tenn.-Ky.	190,232
Pocatello	459,841	Evansville, Ind.-Ky.	205,123
<i>Non-urbanized</i>	608,682	Huntington-Ashland, W.Va.-Ky.-Ohio	483,991
		Lexington-Fayette	1,871,434
		Owensboro	678,634
		<i>Non-urbanized</i>	1,955,756
ILLINOIS:		LOUISIANA:	
<i>Governor's apportionment for areas</i>		<i>Governor's apportionment for areas</i>	
50,000 to 200,000 population	10,975,638	50,000 to 200,000 population	4,005,619
Alton	722,669	Alexandria	711,613
Aurora	1,449,977	Houma	462,826
Beloit, Wis.-Ill.	51,766	Lafayette	1,057,102
Bloomington-Normal	943,789	Lake Charles	913,826
Champaign-Urbana	1,357,578	Monroe	860,252
Danville	473,243	<i>Non-urbanized</i>	1,614,353
Decatur	971,748		
Dubuque, Iowa-Ill.	19,745		
Elgin	1,082,924		
Joliet	1,559,194		
Kankakee	639,637		
Round Lake Beach	504,341		
Springfield	1,199,027		
<i>Non-urbanized</i>	2,523,246		
		MAINE:	
		<i>Governor's apportionment for areas</i>	
		50,000 to 200,000 population	1,729,170
		Bangor	367,130
		Lewiston-Auburn	435,028
		Portland	844,076
		Portsmouth-Dover-Rochester, N.H.-Maine	82,936
		<i>Non-urbanized</i>	705,181
INDIANA:		MARYLAND:	
<i>Governor's apportionment for areas</i>		<i>Governor's apportionment for areas</i>	
50,000 to 200,000 population	6,760,551	50,000 to 200,000 population	1,517,943
Anderson	614,782	Annapolis	549,645
Bloomington	693,836	Cumberland, Md.-W.Va.	440,300
Elkhart-Goshen	697,210	Hagerstown, Md.-Pa.	527,998
Evansville, Ind.-Ky.	1,566,186	<i>Non-urbanized</i>	866,367
Kokomo	635,885		
Lafayette-West Lafayette	993,554		
Muncie	893,351		
Terre Haute	665,747		
<i>Non-urbanized</i>	2,327,051		
		MASSACHUSETTS:	
		<i>Governor's apportionment for areas</i>	
		50,000 to 200,000 population	7,565,099
		Brockton	1,796,287
		Fall River, Mass.-R.I.	1,429,016
		Fitchburg-Leominster	527,785
		Lowell, Mass.-N.H.	1,535,136
		New Bedford	1,546,875
		Pittsfield	403,643
		Taunton	326,357
		<i>Non-urbanized</i>	1,040,942
IOWA:		MICHIGAN:	
<i>Governor's apportionment for areas</i>		<i>Governor's apportionment for areas</i>	
50,000 to 200,000 population	3,770,914	50,000 to 200,000 population	6,731,839
Cedar Rapids	1,179,170	Battle Creek	605,859
Dubuque, Iowa-Ill.	633,129	Bay City	695,318
Iowa City	501,182	Benton Harbor	509,917
Sioux City, Iowa-Nebr.-S.Dak.	626,699	Jackson	722,463
Waterloo	830,734	Kalamazoo	1,313,226
<i>Non-urbanized</i>	1,596,402	Muskegon-Muskegon Heights	865,851
		Port Huron	522,972
		Saginaw	1,496,233
		<i>Non-urbanized</i>	2,803,290
KANSAS:			
<i>Governor's apportionment for areas</i>			
50,000 to 200,000 population	1,620,996		
Lawrence	533,689		
St. Joseph, Mo.-Kans.	8,831		
Topeka	1,078,476		
<i>Non-urbanized</i>	1,215,555		

FISCAL YEAR 1985 UMTA SECTION 9 AND SECTION 18 FORMULA APPORTIONMENTS AMOUNTS APPORTIONED TO AREAS UNDER 200,000 POPULATION—(Continued)

STATE/URBANIZED AREA	APPORTIONMENT	STATE/URBANIZED AREA	APPORTIONMENT
MINNESOTA:		NEW JERSEY:	
Governor's apportionment for areas 50,000 to 200,000 population	\$ 2,286,805	Governor's apportionment for areas 50,000 to 200,000 population	\$ 1,716,512
Duluth-Superior, Minn.-Wis.	682,133	Atlantic City	1,202,718
Fargo-Moorhead, N.Dak.-Minn.	323,287	Vineland-Millville	513,794
Grand Forks, N.Dak.-Minn.	76,704	Non-urbanized	864,448
La Crosse, Wis.-Minn.	32,793		
Rochester	623,722		
St. Cloud	548,166		
Non-urbanized	1,628,684		
MISSISSIPPI:		NEW MEXICO:	
Governor's apportionment for areas 50,000 to 200,000 population	2,168,968	Governor's apportionment for areas 50,000 to 200,000 population	830,083
Biloxi-Gulfport	1,314,635	Las Cruces	442,780
Hattiesburg	400,742	Santa Fe	387,303
Pascagoula-Moss Point	453,591	Non-urbanized	626,312
Non-urbanized	1,556,077		
MISSOURI:		NEW YORK:	
Governor's apportionment for areas 50,000 to 200,000 population	2,673,238	Governor's apportionment for areas 50,000 to 200,000 population	5,472,688
Columbia	486,432	Binghamton	1,531,416
Joplin	381,668	Danbury, Conn.-N.Y.	17,500
St. Joseph, Mo.-Kans.	627,428	Elmira	667,687
Springfield	1,177,710	Glens Falls	394,997
Non-urbanized	1,849,814	Newburgh	489,842
		Poughkeepsie	1,078,323
		Utica-Rome	1,292,923
		Non-urbanized	3,033,154
MONTANA:		NORTH CAROLINA:	
Governor's apportionment for areas 50,000 to 200,000 population	1,934,407	Governor's apportionment for areas 50,000 to 200,000 population	9,378,989
Billings	765,275	Asheville	708,661
Great Falls	667,113	Burlington	503,870
Missoula	502,019	Concord	502,540
Non-urbanized	465,618	Durham	1,387,166
		Gastonia	773,629
		Goldsboro	392,329
		Greensboro	1,555,328
		Hickory	418,370
		High Point	737,446
		Jacksonville	492,872
		Wilmington	599,463
		Winston-Salem	1,307,315
		Non-urbanized	3,125,013
NEBRASKA:		NORTH DAKOTA:	
Governor's apportionment for areas 50,000 to 200,000 population	1,820,643	Governor's apportionment for areas 50,000 to 200,000 population	1,644,380
Lincoln	1,729,893	Bismarck-Mandan	524,040
Sioux City, Iowa-Nebr.-S.Dak.	90,750	Fargo-Moorhead, N.Dak.-Minn.	636,270
Non-urbanized	753,658	Grand Forks, N.Dak.-Minn.	484,070
		Non-urbanized	383,301
NEVADA:		OHIO:	
Governor's apportionment for areas 50,000 to 200,000 population	1,464,378	Governor's apportionment for areas 50,000 to 200,000 population	5,326,321
Reno	1,464,378	Hamilton	965,018
Non-urbanized	165,389	Huntington-Ashland, W.Va.-Ky.-Ohio ..	279,732
NEW HAMPSHIRE:			
Governor's apportionment for areas 50,000 to 200,000 population	2,189,420		
Lowell, Mass.-N.H.	5,339		
Manchester	969,353		
Nashua	663,466		
Portsmouth-Dover-Rochester, N.H.-Maine	551,262		
Non-urbanized	505,466		

**FISCAL YEAR 1985 UMTA SECTION 9 AND SECTION 18 FORMULA APPORTIONMENTS
AMOUNTS APPORTIONED TO AREAS UNDER 200,000 POPULATION—(Continued)**

STATE/URBANIZED AREA	APPORTIONMENT	STATE/URBANIZED AREA	APPORTIONMENT
OHIO—Continued:			
Lima	\$ 613,790	SOUTH CAROLINA:	
Mansfield	607,724	<i>Governor's apportionment for areas</i>	
Middletown	685,881	<i>50,000 to 200,000 population</i>	
Newark	412,834	Anderson	381,020
Parkersburg, W.Va.-Ohio	68,176	Florence	401,385
Sharon, Pa.-Ohio	40,935	Rock Hill	359,219
Springfield	954,214	Spartanburg	712,302
Steubenville-Weirton, Ohio-W.Va.-Pa.	376,243	<i>Non-urbanized</i>	
Wheeling, W.Va.-Ohio	321,774		1,556,284
<i>Non-urbanized</i>	3,430,836	SOUTH DAKOTA:	
OKLAHOMA:		<i>Governor's apportionment for areas</i>	
<i>Governor's apportionment for areas</i>		<i>50,000 to 200,000 population</i>	
<i>50,000 to 200,000 population</i>			1,177,652
Enid	372,302	Rapid City	427,975
Fort Smith, Ark.-Okla.	14,100	Sioux City, Iowa-Nebr.-S.Dak.	12,321
Lawton	773,513	Sioux Falls	737,356
<i>Non-urbanized</i>	1,416,362	<i>Non-urbanized</i>	
OREGON:			444,667
<i>Governor's apportionment for areas</i>		TENNESSEE:	
<i>50,000 to 200,000 population</i>		<i>Governor's apportionment for areas</i>	
Eugene	3,706,638	<i>50,000 to 200,000 population</i>	
Longview, Wash.-Oreg.	1,905,967		2,017,425
Medford	9,759	Bristol, Tenn.-Bristol, Va.	195,679
Salem	466,095	Clarksville, Tenn.-Ky.	370,488
<i>Non-urbanized</i>	1,324,817	Jackson	357,809
	1,099,368	Johnson City	551,487
PENNSYLVANIA:		Kingsport, Tenn.-Va.	541,962
<i>Governor's apportionment for areas</i>		<i>Non-urbanized</i>	
<i>50,000 to 200,000 population</i>			2,017,400
Altoona	10,613,630	TEXAS:	
Erie	819,104	<i>Governor's apportionment for areas</i>	
Hagerstown, Md.-Pa.	2,091,982	<i>50,000 to 200,000 population</i>	
Johnstown	6,783		18,556,838
Lancaster	861,479	Abilene	690,001
Monessen	1,462,661	Amarillo	1,226,886
Reading	506,617	Beaumont	931,266
Sharon, Pa.-Ohio	1,952,038	Brownsville	959,046
State College	449,423	Bryan-College Station	659,565
Steubenville-Weirton, Ohio-W.Va.-Pa.	612,006	Galveston	536,539
Williamsport	1,873	Harlingen-San Benito	515,657
York	565,016	Killeen	786,285
<i>Non-urbanized</i>	1,284,648	Laredo	1,260,572
	3,782,198	Longview	494,548
PUERTO RICO:		Lubbock	1,443,414
<i>Governor's apportionment for areas</i>		McAllen-Pharr-Edinburg	1,500,013
<i>50,000 to 200,000 population</i>		Midland	607,011
Aguadilla	7,415,680	Odessa	916,460
Arecibo	593,324	Port Arthur	827,111
Caguas	679,573	San Angelo	620,847
Mayaguez	1,591,575	Sherman-Denison	383,852
Ponce	1,114,570	Temple	354,292
Vega Baja-Manati	2,619,528	Texarkana, Tex.-Ark.	338,825
<i>Non-urbanized</i>	817,110	Texas City-La Marque	682,733
	1,189,688	Tyler	623,772
RHODE ISLAND:		Victoria	487,205
<i>Governor's apportionment for areas</i>		Waco	933,798
<i>50,000 to 200,000 population</i>		Wichita Falls	777,140
Fall River, Mass.-R.I.	590,068	<i>Non-urbanized</i>	
Newport	128,553		4,108,567
<i>Non-urbanized</i>	461,515		
	125,931		

**FISCAL YEAR 1985 UMTA SECTION 9 AND SECTION 18 FORMULA APPORTIONMENTS
AMOUNTS APPORTIONED TO AREAS UNDER 200,000 POPULATION—(Continued)**

STATE/URBANIZED AREA	APPORTIONMENT	STATE/URBANIZED AREA	APPORTIONMENT
UTAH:		WEST VIRGINIA—Continued:	
Governor's apportionment for areas 50,000 to 200,000 population	\$ 1,503,979	Huntington-Ashland, W.Va.-Ky.-Ohio	\$ 912,444
Provo-Orem	1,503,979	Parkersburg, W.Va.-Ohio	600,280
Non-urbanized	331,364	Steubenville-Weirton, Ohio-W.Va.-Pa.	238,036
		Wheeling, W.Va.-Ohio	689,409
		Non-urbanized	1,245,470
VERMONT:		WISCONSIN:	
Governor's apportionment for areas 50,000 to 200,000 population	586,413	Governor's apportionment for areas 50,000 to 200,000 population	8,801,229
Burlington	586,413	Appleton	1,472,307
Non-urbanized	350,321	Beloit, Wis.-Ill.	383,770
		Duluth-Superior, Minn.-Wis.	172,554
VIRGINIA:		Eau Claire	573,230
Governor's apportionment for areas 50,000 to 200,000 population	4,203,228	Green Bay	1,113,255
Bristol, Tenn.-Bristol, Va.	152,308	Janesville	465,039
Charlottesville	624,030	Kenosha	1,064,126
Danville	439,696	La Crosse, Wis.-Minn.	617,347
Kingsport, Tenn.-Va.	29,444	Oshkosh	552,981
Lynchburg	615,322	Racine	1,354,801
Petersburg-Colonial Heights	844,176	Sheboygan	577,265
Roanoke	1,498,252	Wausau	454,554
Non-urbanized	1,854,473	Non-urbanized	1,908,239
WASHINGTON:		WYOMING:	
Governor's apportionment for areas 50,000 to 200,000 population	3,542,365	Governor's apportionment for areas 50,000 to 200,000 population	1,105,266
Bellingham	429,809	Casper	588,877
Bremerton	527,785	Cheyenne	516,389
Longview, Wash.-Oreg.	420,790	Non-urbanized	283,397
Olympia	531,444		
Richland-Kennewick	866,936	AMERICAN SAMOA:	
Yakima	765,601	Non-urbanized	26,014
Non-urbanized	1,216,820		
WEST VIRGINIA:		GUAM:	
Governor's apportionment for areas 50,000 to 200,000 population	3,870,711	Non-urbanized	85,363
Charleston	1,409,599		
Cumberland, Md.-W.Va.	20,943	NORTHERN MARIANA ISLANDS:	
		Non-urbanized	13,516
		VIRGIN ISLANDS:	
		Non-urbanized	77,783

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Best Interest Federal

Friday
October 26, 1984

Part VII

Department of Education

34 CFR Part 760

Secretary's Discretionary Program; Final
Regulations

DEPARTMENT OF EDUCATION

34 CFR Part 760

Secretary's Discretionary Program

AGENCY: Department of Education.

ACTION: Final regulations.

SUMMARY: The Secretary issues regulations for the implementation of the Secretary's Discretionary Program. The Secretary's Discretionary Program supports research, demonstration, dissemination, training, and technical assistance projects designed to meet special educational needs of educationally deprived children or to improve elementary and secondary education for children consistent with the purposes of the Education Consolidation and Improvement Act of 1981.

DATE: These regulations will take effect either 45 days after they are published in the *Federal Register* or later if Congress takes certain adjournments. If you want to know the effective date of these regulations, write or call the Department of Education contact person.

FOR FURTHER INFORMATION CONTACT: Dr. Thomas E. Enderlein, 400 Maryland Avenue, SW., Room 4181, Washington, D.C. 20202. Telephone: (202) 472-1762.

SUPPLEMENTARY INFORMATION:**Background**

The Education Consolidation and Improvement Act of 1981 (ECIA) (20 U.S.C. 3801 *et seq.*) was enacted as Title V of the Omnibus Budget Reconciliation Act of 1981 (Pub. L. 97-35). The ECIA has two principal purposes: Chapter 1 provides financial assistance to State and local educational agencies (SEA's and LEA's) to meet the special needs of educationally deprived children, and Chapter 2 consolidates 28 elementary and secondary level education grant programs into a single authorization of grants to States for the same purposes contained in the consolidated programs.

Section 583(a) of Chapter 2 authorizes the Secretary to carry out directly, or through grants or contracts, programs and projects that: (1) Provide a national source for gathering and disseminating information on the effectiveness of programs designed to meet the special educational needs of educationally deprived children and others served by the ECIA, and for assessing the needs of such individuals; (2) carry out research and demonstrations related to the purposes of the ECIA; (3) are designed to improve the training of teachers and other instructional personnel needed to carry out the purposes of the ECIA; or

(4) are designed to assist SEA's and LEA's in the implementation of programs under the ECIA.

Public Comments

The Secretary published in the *Federal Register* on February 29, 1984 (49 FR 7546), a Notice of Proposed Rulemaking (NPRM) and invited public comment on the proposed regulations. A summary of all substantive comments received on the NPRM and the Secretary's response can be found in the Appendix to these final regulations.

Summary of Changes From the NPRM

Only one change was made in the final regulations after the review of the NPRM. Section 760.11(e) has been revised to clarify that the Secretary may decline to fund a project that is eligible for funding under another "specific Department of Education grant competition." This provision implements the Secretary's policy to use limited resources available under the Discretionary Program for activities that cannot be assisted under other grant competitions.

Summary of Major Provisions**(1) Projects Eligible for Funding**

Section 760.10 implements the statutory restrictions on the types of projects that may be funded under the Secretary's Discretionary Program. To be eligible for funding under this program, a project must relate to the purposes of the ECIA, and must be limited to one or more of the following: gathering and disseminating information, assessing the effectiveness of programs, research, demonstration, training of teachers or other instructional personnel, or technical assistance to SEA's or LEA's.

Section 583 of the ECIA does not authorize the Secretary to provide general operating revenue to any applicant, including a local school district, an institution of higher education, or other agencies that need or wish additional resources to meet local needs.

(2) Establishing Priorities

Section 760.11 of the regulations permits the Secretary to announce funding priorities for the Discretionary Program in one or more notices published in the *Federal Register* each year. The regulations incorporate the statutorily broad discretion of the Secretary in order to permit the Secretary to exercise leadership in education by focusing national attention on unmet national needs within the educational areas addressed by the ECIA.

Under the final regulations, the Secretary would select funding priorities by taking into consideration any unmet national needs within the scope of the ECIA. For example, in fiscal year 1983, the Secretary established as funding priorities for this program: (1) Expanding parental choice in education, (2) improving teacher quality through incentives, (3) strengthening local school boards, and (4) improving education through the application of technology. For fiscal year 1984, the Secretary has made planning teacher incentive structures a funding priority for this program. See "Notice of Final Annual Funding Priorities, Required Activities, and Geographical Distribution for Fiscal Year 1984" published in 48 FR 56257 (December 20, 1983).

In addition to or instead of establishing funding priorities, the Secretary could invite applicants to propose projects in any area of education within the purposes of the ECIA. For example, in fiscal year 1983, the Secretary funded unsolicited applications on topics that included follow-up activities to the National Commission on Excellence in Education, literacy in the school-age population, school violence, and training school board members in the area of special education.

The ECIA generally addresses meeting the special educational needs of educationally deprived children and improving elementary and secondary education for children. However, also included within the scope of the ECIA are the purposes of the programs consolidated in section 561 of the ECIA. Accordingly, subject to other requirements of the ECIA and the final regulations, the Secretary could fund any project that would involve the same activities as formerly authorized by one of the programs consolidated into the ECIA, some of which included specific activities beyond the elementary and secondary level.

For example, the Secretary could fund a demonstration project on consumer education that benefitted the public as a whole because consumer education was authorized to be provided to the public under Title III, Part E of the Elementary and Secondary Education Act (ESEA), one of the authorities consolidated into the ECIA.

The only exception is that although Title II of the ESEA authorized activities beyond the elementary and secondary education level, Chapter 2 of the ECIA limits basic skills to activities relating to elementary and secondary school instruction.

(3) Selection Criteria

Section 760.31 of the regulations establishes selection criteria for this program and indicates the maximum number of points that an application could score for each criterion. Additionally, under 760.30, the Secretary will distribute a reserved 15 points among the criteria for each grant competition. The Secretary will announce, in a notice published in the *Federal Register*, how the reserved points would be distributed for each competition.

(4) Geographical Distribution

Under § 760.32 of the regulations, the Secretary could fund applications other than the most highly rated applications if doing so would improve the geographical distribution of projects receiving funding in a particular competition.

(5) Private School Children Participation

Section 760.20 requires an LEA to provide an assurance that it will comply with the provisions of section 586 of the ESEA, governing the equitable participation of private school children, if the LEA submits an application for funding to provide services, materials, or equipment for the benefit of public school students. Specific requirements are established in EDGAR, 34 CFR 75.650. Applicants other than LEA's as described above are not subject to the equitable participation requirements in section 586 of the ESEA or in EDGAR.

(6) Scope of the Final Regulations

Under § 760.3, the regulations will apply to grants awarded under the Secretary's Discretionary Program, except for grants awarded under any grant program, such as the National Diffusion Network, for which the Secretary issues separate regulations. The regulations do not apply to contracts awarded under the Secretary's Discretionary Program.

Executive Order 12291

These regulations have been reviewed in accordance with Executive Order 12291.

They are classified as non-major because they do not meet the criteria for major regulations established in the Order.

Paperwork Reduction Act of 1980

Information collection requirements contained in these regulations (Sections 760.20; 760.30-760.32) have been approved by the Office of Management and Budget under the provisions of the Paperwork Reduction Act of 1980 (Pub.

L. 96-511) and have been assigned OMB Control No. 1880-0505. This control number appears as a citation at the end of each applicable section.

Assessment of Educational Impact

In the notice of proposed rulemaking, the Secretary requested comments on whether the proposed regulations would require transmission of information that is being gathered by or is available from any other agency or authority of the United States.

Based on the comments on the proposed rules and the Department's own review, it has been determined that the regulations in this document do not require information that is being gathered by or is available from any other agency or authority of the United States.

List of Subjects in 34 CFR Part 760

Education, Education of disadvantaged, Elementary and secondary education. Grant programs—education. Reporting and recordkeeping requirements.

Citation of Legal Authority

A citation of statutory or other legal authority is placed in parentheses on the line following each substantive provision of these final regulations.

Dated: October 22, 1984.

(Catalog of Federal Domestic Assistance Number 84.122, Secretary's Discretionary Program)

T.H. Bell,

Secretary of Education.

The Secretary amends Title 34 of the Code of Federal Regulations by adding a new Part 760 to read as follows:

PART 760—SECRETARY'S DISCRETIONARY PROGRAM**Subpart A—General**

Sec.

760.1 What is the Secretary's Discretionary Program?

760.2 Who is eligible for a grant under the Secretary's Discretionary Program?

760.3 What regulations apply to the Secretary's Discretionary Program?

760.4 What definitions apply to this program?

Subpart B—What Types of Projects Does the Secretary Assist Under This Program?

760.10 What types of projects does the Secretary assist under this program?

760.11 Does the Secretary establish priorities for this program?

Subpart C—How Does One Apply for a Grant?

760.20 What assurance must an applicant make?

Subpart D—How Does the Secretary Make a Grant?

Sec.

760.30 How does the Secretary evaluate an application?

760.31 What selection criteria does the Secretary use?

760.32 How does the Secretary select an application for funding?

Subpart E—What Conditions Must Be Met by the Grantee?

760.40 May the Secretary restrict the use of funds under this program?

760.41 May program funds be used for construction purposes?

Authority: Sec. 583 of the Education Consolidation and Improvement Act of 1981 (20 U.S.C. 3851), unless otherwise noted.

Subpart A—General**§ 760.1 What is the Secretary's Discretionary Program?**

The Secretary's Discretionary Program supports projects designed to meet the special educational needs of educationally deprived children or to improve elementary and secondary education for children consistent with the purposes of the Education Consolidation and Improvement Act of 1981.

(20 U.S.C. 3851)

§ 760.2 Who is eligible for a grant under the Secretary's Discretionary Program?

State educational agencies (SEA's), local educational agencies (LEA's), institutions of higher education, and other public and private agencies, organizations, and institutions are eligible for a grant under the Secretary's Discretionary Program.

(20 U.S.C. 3851)

§ 760.3 What regulations apply to the Secretary's Discretionary Program?

(a) The following regulations apply to grants made under the Secretary's Discretionary Program:

(1) The Education Department General Administrative Regulations (EDGAR) established in Title 34 of the Code of Federal Regulations in Part 74 (Administration of Grants), Part 75 (Direct Grant Programs), Part 77 (Definitions), and Part 78 (Education Appeal Board).

(2) The regulations in this Part 760.

(b) The regulations in this Part 760 do not apply to—

(1) Contracts awarded under the Secretary's Discretionary Program; and

(2) Grants and contracts awarded under any grant program, such as the National Diffusion Network, for which the Secretary issues separate regulations.

Note.—Grants awarded under the National Diffusion Network are subject to the regulations in 34 CFR Part 796.
(20 U.S.C. 3851; 3474)

§ 760.4 What definitions apply to this program?

(a) *Definitions in EDGAR.* The following terms used in these regulations are defined in 34 CFR Part 77:

Applicant
Application
Award
Budget
Department
EDGAR
Local educational agency
Minor remodeling
Nonprofit
Private
Project
Public
Secretary
State education agency

(b) *Definitions that apply to this Part.* The following definitions apply to this Part:

"Children" means persons—
(1) Up to age 21 who are entitled to a free public education not above grade 12; or
(2) Who are of preschool age.
"Construction" means the preparation of drawings and specifications for school facilities; erecting, building, acquiring, altering, remodeling, improving, or extending school facilities; and the inspection and supervision of the construction of school facilities.
(20 U.S.C. 3875)

"ECIA" means Education Consolidation and Improvement Act of 1981.

"Educationally deprived children" means children whose educational attainment is below the level that is appropriate for children of their age.
(20 U.S.C. 3851; 3474)

Subpart B—What Types of Projects Does the Secretary Assist Under This Program?

§ 760.10 What types of projects does the Secretary assist under this program?

(a) The Secretary may fund projects that—
(1) Provide a national source for gathering and disseminating information on the effectiveness of programs designed to meet the special educational needs of educationally deprived children and others served by the ECIA, and for assessing the needs of such individuals;
(2) Carry out research and demonstrations related to the purposes of the ECIA;

(3) Are designed to improve the training of teachers and other instructional personnel needed to carry out the purposes of the ECIA; or
(4) Provide technical assistance to SEA's and LEA's in the implementation of programs under the ECIA.

(b) The Secretary may not provide general operating revenue to meet local needs to any applicant under this program.
(20 U.S.C. 3851)

§ 760.11 Does the Secretary establish priorities for this program?

(a) Each year, through one or more notices published in the *Federal Register*, the Secretary announces the priorities for this program, if any, and the manner in which those priorities will be implemented.

(b) The Secretary selects priorities by taking into consideration unmet national needs within the scope of the ECIA.

(c) The Secretary may also fund any project that does not meet an established priority if the project—

(1) Is limited to activities—
(i) That are at the elementary or secondary education level; or
(ii) That were specifically authorized by one of the programs consolidated in the ECIA as listed in section 561 of the ECIA except as limited by the ECIA; and
(2) Satisfies all other requirements for funding under this program.

(d) If the Secretary selects priorities, the Secretary may establish a separate competition for each priority selected. If a separate competition is established for a priority, the Secretary may reserve all applications that relate to that priority for review under the separate competition.

(e) The Secretary may decline to fund a project that is eligible for funding under a specific Department of Education grant competition.

Note.—EDGAR establishes the method for applying priorities. See 34 CFR 75.105 (Annual priorities).
(20 U.S.C. 3851; 3474)

Subpart C—How Does One Apply for a Grant?

§ 760.20 What assurance must an applicant make?

An applicant must make an assurance in its application that it will comply with the provisions of section 586 of the ECIA, governing equitable participation of private school children in the purposes and benefits of Chapter 2, if the applicant—

(a) Is an LEA; and
(b) Proposes to use grant funds to provide—for the benefit of public school students—services, materials, or

equipment (including training for teachers or other personnel serving the school children).

Note.—EDGAR establishes requirements for private school children participation. See 34 CFR 75.650.

(20 U.S.C. 3882)

(Approved by the Office of Management and Budget under control number 1880-0505)

Subpart D—How Does The Secretary Make a Grant?

§ 760.30 How does the Secretary evaluate an application?

(a) The Secretary evaluates an application submitted under this program on the basis of the criteria in § 760.31 of this part.

(b) The Secretary may award up to 100 points, including a reserved 15 points to be distributed in accordance with paragraph (d) of this section, based on the criteria in § 760.31.

(c) Subject to paragraph (d) of this section, the maximum possible points for each criterion is indicated in parentheses after the heading for each criterion.

(d) For each competition, as announced through a notice published in the *Federal Register*, The Secretary may distribute the reserved 15 points among the criteria listed in § 760.31.

(20 U.S.C. 3851; 3774)

(Approved by the Office of Management and Budget under control number 1880-0505)

§ 760.31 What selection criteria does the Secretary use?

The Secretary uses the following criteria in evaluating each application:

(a) *Plan of operation.* (20 points)
(1) The Secretary reviews each application for information that shows the quality of the plan of operation for the project.

(2) The Secretary looks for information that shows—

(i) High quality in the design of the project;

(ii) An effective plan of management that insures proper and efficient administration of the project;

(iii) A clear description of how the objectives of the project relate to the purposes of the program;

(iv) The way the applicant plans to use its resources and personnel to achieve each objective;

(v) A clear description of how the applicant will provide equal access and treatment for eligible project participants who are members of groups that have been traditionally underrepresented, such as—

(A) Members of racial or ethnic minority groups;

(B) Women;

(C) Handicapped persons; and

(D) The elderly; and

(vi) For applicants required to provide an opportunity for participation of students enrolled in private schools—a clear description of how the applicant will provide that opportunity.

(b) *Quality of key personnel.* (15 Points)

(1) The Secretary reviews each application for information that shows the quality of the key personnel the applicant plans to use on the project.

(2) The Secretary looks for information that shows—

(i) The qualifications of the project director (if one is to be used);

(ii) The qualifications of each of the other key personnel to be used in the project;

(iii) The time that each person referred to in paragraphs (b)(2)(i) and (ii) of this section plans to commit to the project;

(iv) The extent to which the applicant, as a part of its nondiscriminatory employment practices, encourages applications for employment from persons who are members of groups that have been traditionally underrepresented, such as—

(A) Members of racial or ethnic minority groups;

(B) Women;

(C) Handicapped persons; and

(D) The elderly.

(3) To determine the qualifications of a person, the Secretary considers evidence of past experience and training, in fields related to the objectives of the project, as well as other information that the applicant provides.

(c) *Budget and cost effectiveness.* (5 Points)

(1) The Secretary reviews each application for information that shows that the project has an adequate budget and is cost effective.

(2) The Secretary looks for information that shows—

(i) The budget for the project is adequate to support the project activities; and

(ii) Costs are reasonable in relation to the objectives of the project.

(d) *Evaluation plan.* (5 Points)

(1) The Secretary reviews each application for information that shows the quality of the evaluation plan for the project. Cross-reference—See EDGAR 34 CFR 75.590 (Evaluation by the grantee).

(2) The Secretary looks for information that shows methods of evaluation that are appropriate for the project and, to the extent possible, are

objective and produce data that are quantifiable.

(e) *Adequacy of resources.* (5 Points)

(1) The Secretary reviews each application for information that shows that the applicant plans to devote adequate resources to the project.

(2) The Secretary looks for information that shows—

(i) The facilities that the applicant plans to use are adequate; and

(ii) The equipment and supplies that the applicant plans to use are adequate.

(f) *Improving elementary and secondary education.* (10 Points)

(1) The Secretary reviews each application for information that shows the extent to which the project contributes to the improvement of elementary and secondary education.

(2) The Secretary looks for information such as—

(i) The objectives of the project; and

(ii) The manner in which the objectives of the project further the purpose of improving elementary and secondary education.

(g) *National significance.* (15 Points)

(1) The Secretary reviews each application for information that shows the national significance of the project.

(2) The Secretary looks for information that shows the extent to which the project makes a contribution of national significance, as measured by factors such as—

(i) The extent to which the project addresses educational problems of national significance;

(ii) The extent to which the project meets specific national needs as shown by—

(A) The needs addressed by the project;

(B) The manner in which the applicant identified those needs;

(C) The manner in which those needs are met by the project; and

(D) The benefits to be gained by meeting those needs;

(iii) The extent to which the project involves techniques that are innovative;

(iv) The extent to which the project builds upon and adds to current educational information and research; and

(v) The extent to which the project provides a model or other information that could be used by others to solve educational problems.

(h) *Applicant's commitment and capacity.* (10 Points)

The Secretary looks for information that shows the extent of the applicant's commitment to the project, its capacity to continue the project, and the likelihood that it will build upon the project when Federal assistance ends.

(20 U.S.C. 3851; 3474)

(Approved by the Office of Management and Budget under control number 1880-0505)

§ 760.32 How does the Secretary select an application for funding?

(a) After evaluating the applications according to the criteria contained in § 760.31, the Secretary may determine whether or not the most highly rated applications are broadly and equitably distributed throughout the Nation for each competition.

(b) The Secretary may select other applications for funding if doing so would improve the geographical distribution of projects funded under a particular competition.

(20 U.S.C. 3851; 3474)

(Approved by the Office of Management and Budget under control number 1880-0505)

Subpart E—What Conditions Must Be Met by the Grantee?

§ 760.40 May the Secretary restrict the use of funds under this program?

The Secretary may restrict the amount of funds made available through a grant under this program that may be used to purchase equipment.

(20 U.S.C. 3851)

§ 760.41 May program funds be used for construction purposes?

(a) No recipient may use grant funds for repairs, minor remodeling, or construction of private school facilities.

(b) To the extent necessary for an LEA to carry out its responsibility under section 596 of the ECIA to provide an opportunity for the equitable participation of private school children, an LEA may use grant funds for the construction of public facilities.

(c) Subject to the restrictions in paragraph (a) of this section, a recipient may use grant funds for repairs or minor remodeling only to the extent necessary to carry out an approved project under the regulations in this part.

(20 U.S.C. 3851; 3474)

Note.—This Appendix will not appear in the Code of Federal Regulations.

Appendix—Comments and Responses from NPRM

The following is a summary of the public comments received on the proposed regulations published on February 29, 1984 (49 FR 7546), and the Secretary's responses to those comments. Generally, the comments are presented according to the numbered order of the regulations.

During the 45 days allowed for comment, two letters and one informal response were received. The commenters generally requested

clarification of specific provisions of the regulations. However, one commenter, the Chicago Board of Education (Chicago)—in addition to making many of the specific comments summarized below—characterized the proposed rules as “a blatant misuse, if not abuse, of the administrative rulemaking powers delegated to the Department.”

Chicago contended in its letter that one of the main “purposes of the proposed rules, if not the sole purpose, appears to be preventing the Chicago Board of Education from securing funding from the Discretionary Fund for implementation of its desegregation plan pursuant to the obligations of the Board and the United States under the Consent Decree of September 24, 1980.” Chicago further stated, “The Department is attempting to accomplish through its rulemaking process what it cannot accomplish before a neutral judicial forum. . . . This is certainly a morally questionable and quite possibly a constitutionally questionable use of the power of the United States against a local Board of Education.” Finally, after making many other comments (which are summarized below) on specific sections of the regulations, Chicago recommended “that this entire set of flawed regulations be redrafted pursuant to these comments and issued again in proposed form.”

The rules of general applicability established by these final regulations—including the rules for selecting priorities and the selection criteria—are needed to govern competitive awards of grants with Discretionary Program funds. These regulations have been promulgated in accordance with the rulemaking requirements of section 431 of the General Education Provisions Act, 20 U.S.C. 1232, and of the Administrative Procedure Act, 5 U.S.C. 553, and are consistent with established statutory interpretations and practices under the Discretionary Program. See, for example, “The Secretary’s Discretionary Program—Planning Grants to Develop Teacher Incentive Structures,” 48 FR 56257 (December 20, 1983).

These regulations are not motivated by any attempt to deprive Chicago or any other potential applicant of its right to compete for funds under the statute. On the contrary, the Secretary is issuing these final regulations in accordance with the statute and its legislative history, as consistently interpreted by the Department since the beginning of this program.

General

Comment. One commenter questioned the Secretary’s authority to issue regulations under the Secretary’s

Discretionary Program. The commenter cited section 591 of the ECIA, which authorizes the Secretary to issue regulations “relating to the discharge of duties specifically assigned to the Secretary under [the ECIA],” and which prohibits the Secretary from issuing regulations “in all other matters relating to the details of planning, developing, implementing, and evaluating programs and projects by State and local educational agencies * * *.”

Response. No change has been made. In establishing the Secretary’s Discretionary Program, section 583 of the ECIA specifically assigns to the Secretary the duty of carrying out the authorized activities directly or through grants or contracts. Beyond indicating in broad terms the types of activities that are eligible for funding, the statute does not prescribe the priorities, evaluation criteria, or procedures to be used by the Secretary in making these funding decisions. These are matters for the Secretary to determine under section 583, as opposed to details of State and local administration of programs. These regulations clearly are authorized by section 591.

Subpart A—General

Section 760.3(a)(1) What regulations apply to the Secretary’s Discretionary Program?

Comment. One commenter questioned why the Secretary’s Discretionary Program is not subject to 34 CFR Part 79, the implementing regulations for Executive Order 12372 (Intergovernmental Review of Federal Programs). The commenter contended that, in some cases, projects assisted under the Secretary’s Discretionary Program may be of special interest to States.

Response. No change has been made. The Secretary’s Discretionary Program is excluded from coverage under 34 CFR Part 79 because its purpose is not to support services to particular State or local jurisdictions, nor is it directly relevant to the governmental responsibilities of a State or local government. Nevertheless, as a courtesy in a case such as that described by the commenter, the Secretary may choose to notify the State single points of contact of competitions that may be of special interest to States.

Comment. One commenter noted that the regulations in 34 CFR Part 760 do not apply to contracts awarded under the Secretary’s Discretionary Program and asked what regulations do apply.

Response. No change has been made. Contracts awarded after April 1, 1984 are subject to the government-wide

Federal Acquisition Regulations, 48 CFR Chapter 1. Additionally, the Department will issue its own implementing regulations in the near future.

Subpart B—What Types of Projects Does the Secretary Assist under This Program?

Section 760.10 What types of projects does the Secretary assist under this program?

Comment. One commenter recommended that the language in proposed §§ 760.10(a) and 760.11(c) be changed to include “programs” as well as “projects” as being eligible for funding.

Response. No change has been made. Only the term “project” is used in the above-cited provisions of the final regulations to ensure consistency of terminology throughout the Department’s regulations. In 34 CFR 77.1, “project” is defined as “the activity described in an application.” In essence, a “project” consists of the specific activities that the Department assists. Nevertheless, those activities—if otherwise eligible—may be part of one or more larger programs conducted by a grantee.

Comment. One commenter questioned the use of the term “technical assistance” in § 760.10(a)(4), in describing the types of projects that may be funded under the Secretary’s Discretionary Program. The commenter pointed out that section 583 of the ECIA authorizes the Secretary to carry out programs and projects which “are designed to assist State and local educational agencies in the implementation of programs under [the ECIA].”

Response. No change has been made. The term “technical assistance” reflects an interpretation of the activities Congress intended to authorize in section 583(a)(4) of the ECIA. The specific language of section 583(a)(4) supports this interpretation in that it authorizes projects which “* * * assist State and local educational agencies in the implementation of programs under [the ECIA].” Under section 583(a)(4), projects are eligible only if they assist programs funded under the ECIA. The only logical reading of this authority is as a technical assistance provision to help improve State and local programs receiving funds under other parts of the ECIA. The legislative history of the ECIA also supports the Department’s conclusion that Congress, in section 583(a)(4), intended to assist activities in the nature of technical assistance to State and local educational agencies,

not direct funding of State and local programs. The Senate committee report on the language in the Senate Bill, which was enacted as the ECIA, provided: "Up to five percent of the funds under subpart 2 may be used at the discretion of the Secretary for national dissemination activities, research and demonstration programs, and technical assistance programs." S. Rep. 97-139, 97th Cong., 1st Sess. 897 (1981).

Comment. One commenter objected to the provision prohibiting the Secretary from providing operating revenue to meet local needs to any applicant under this program. The commenter argued that (1) rarely, if ever, does an applicant for a Federal grant propose a project for support which does not address a local need, (2) the purpose of the ECIA is to meet the special needs of certain categories of children, and (3) the grant assistance either adds to, or provides all of, the operating revenue to implement a grant project.

Response. No change has been made. The Secretary has consistently interpreted section 583 of the ECIA as not authorizing the Department to make a grant to an LEA or other applicant for general operating support. This is expressly authorized only by sections 561-582 of Chapter 2 of the ECIA (20 U.S.C. 3811-3842), governing funds allocated by formula to LEA's or reserved for State use. It would have been illogical for Congress to have established an authority for very limited direct funding by the Secretary at the national level—with a maximum of 6 percent of Chapter 2 funds—if that authority were to be used for direct funding to meet the general operating needs of a particular school district, thereby duplicating the authorized uses for the 94 percent of Chapter 2 funds allocated to the States. In fact, Congress did not intend to do so. The nature of the activities specifically authorized by section 583, including the mandated programs in section 583(b); the level of funds authorized; the overall structure of Chapter 2 of the ECIA; the consistent practice under section 583 and its antecedent authority, section 303(a) of the Elementary and Secondary Education Act of 1965 (20 U.S.C. 2943); and the legislative history of section 583 all lead to this conclusion.

Section 760.10(b) is consistent with previous notices for competitions under the Secretary's Discretionary Program which the Department has issued. See Application Notice for the Secretary's Discretionary Program Planning Grants to Develop Teacher Incentive Structures (48 FR 56257, December 20, 1983 at 56258, "Funding for projects under these

grants will be limited to the cost of developing a workable plan."); Application Notice for the Secretary's Discretionary Program Grants—Improving Education through the Application of Technology (48 FR 30080, June 29, 1983 at 30081, "Funding under these awards will cover the cost of planning, administering, evaluating, and disseminating information about the project."); Application Notice for the Secretary's Discretionary Program Grants (48 FR 13220, March 30, 1983 at 13221, "Funding for demonstration projects under these awards will be limited to the cost of administering and evaluating the project," and at 13222, "Funding for projects under these awards will be limited to the cost of collecting and analyzing information to describe and assess the effects of the demonstration," and "Funding of projects under this award will not include stipends or travel costs for trainees.")

Moreover, the Catalog of Federal Domestic Assistance (CFDA) lists the Secretary's Discretionary Program, beginning with the 1983 update, and indicates in the description of "uses and use restrictions" that "[n]o awards can be made to provide general operating support to a local educational agency (LEA) or other eligible applicants." See CFDA No. 84.122. The CFDA—which is published by the Executive Office of the President, Office of Management and Budget—is a basic source of information on Federal programs and has as its primary purpose assisting potential applicants to identify Federal programs for which they may apply, and providing general information on these programs. See similar provisions, making operating costs ineligible for support under other research and demonstration programs in 34 CFR 709.12, 710.6, 716.11, 718.6, and 720.6.

Section 760.11(b) Does the Secretary establish priorities for this program?

Comment. One commenter objected to the provision which provides for the Secretary to select priorities by taking into consideration unmet national needs and asserted that the Secretary may not disable himself from the discretion to fund any project authorized by the statute. The commenter noted that the ECIA makes the Secretary's Discretionary Program funds available to support projects which relate to the purposes of the ECIA.

Response. No change has been made. The Secretary has the authority to issue regulations "relating to the discharge of the Secretary's duties specifically assigned under [the ECIA]." 20 U.S.C. 3871(a). One of those duties is to

determine how monies appropriated by Congress for the Discretionary Program are spent. In carrying out this duty, consistently with the purposes of the Discretionary Program, the Secretary sets priorities for distribution of monies "taking into consideration unmet national needs within the scope of the ECIA." Selecting priorities does not preclude the Secretary from funding a project that does not meet an established priority provided that the project is within the scope of the ECIA and satisfies the requirements for funding described in the statute; namely, a project which relates to the purposes of the ECIA and the Discretionary Program's national perspective, and which involves dissemination of information, research, demonstration, training of instructional personnel, or technical assistance to State and local educational agencies.

Comment. One commenter questioned whether proposed § 760.11(c)(1)(ii) limits funding under the Secretary's Discretionary Program to those activities which are allowable under programs consolidated into the ECIA, and argued that the purposes and authorized activities contained in the ECIA itself are the controlling authority for permissible activities under the Secretary's Discretionary Program.

Response. No change has been made. Each of the activities specifically authorized by section 583(a)—namely, dissemination of information, research, demonstration, the training of instructional personnel, or technical assistance for State or local educational agencies—is tied by the language of section 583 to the purposes of the subtitle, children served by the subtitle, or programs under the subtitle. The subtitle is Subtitle D of the Omnibus Education Reconciliation Act of 1981 and includes Chapters 1 and 2 of the ECIA. As interpreted by the Secretary, the purposes and activities of the subtitle include—in addition to Chapter 1 programs—all of the purposes and activities that previously could have been funded under the antecedent programs consolidated by Chapter 2, except to the extent inconsistent with specific language in Chapter 2.

The only such inconsistency is that although the former basic skills program under Title II of the Elementary and Secondary Education Act authorized activities beyond the elementary and secondary level, Chapter 2 of the ECIA specifically limits basic skills activities to those relating to elementary and secondary school instruction. Of course, as indicated above, projects may be funded under the Secretary's

Discretionary Program only if they meet the specific authorizations in section 583.

Comment. One commenter questioned whether § 760.11(e) should enable the Secretary to decline to fund a project that is eligible for funding under another Department of Education program. The commenter noted that every activity eligible for support under the Secretary's Discretionary Program, by definition, can be funded under the Chapter 1 or Chapter 2 (block grant programs) of the ECIA.

Response. A change has been made. Section 760.11(e) has been revised to permit the Secretary to decline to fund a project that is eligible for funding under another "specific Department of Education grant competition." This change should eliminate the problem raised by the commenter while still carrying out the Secretary's policy of using limited resources available under the Discretionary Program for worthwhile activities that cannot be assisted under other grant competitions.

Subpart D—How Does the Secretary Make a Grant?

Section 760.31 What selection criteria does the Secretary use?

Comment. One commenter recommended that the Secretary delete the selection criterion related to the national significance of a project in proposed § 760.31(g). The commenter contended that any project which relates to the purposes of the ECIA may be funded. The commenter suggested that in an instance where national significance is an appropriate criterion, the Secretary could assign part of the reserved 15 points to that criterion.

Response. No change has been made. As noted above in response to a comment on § 760.11(b), § 760.11(c) permits the Secretary to fund any project that is within the scope of the

ECIA and that involves dissemination of information, research, demonstration, training of instructional personnel, or technical assistance to State or local educational agencies related to programs implemented under the ECIA.

Chapter 2 of the ECIA essentially converted the categorical antecedent programs into State and local programs and reserved a small amount of appropriated funds for the Secretary to use under the Discretionary Program in identifying significant programs from a national perspective. Use of the criterion of "national significance" in making awards is designed to identify those projects which best carry out the purposes of the Discretionary Program. This criterion has been consistently used in selecting applications for funding under this program. The Catalog of Federal Domestic Assistance (CFDA) describes the objectives of the Secretary's Discretionary Program "to assist in research, dissemination, demonstration, improvement of training, and technical assistance activities, which address some national education priority as authorized by Section 583 of the [ECIA]." See CFDA No. 84.122.

Comment. One commenter questioned the usefulness of the capacity to continue a project as a criterion for evaluating an application for funds in view of the fact that there may be no need to continue some types of projects, for example, a teacher training project.

Response. No change has been made. Section 760.32(h) provides for the Secretary, in selecting applications for funding, to consider the extent of the applicant's commitment to, and capacity to continue, a project, as well as the likelihood that the applicant will build upon the project when Federal assistance ends. While the training phase of a project, for example, may end, the continued use of the training by those individuals that received it is a

measure of the impact and usefulness of the project.

Section 760.32 How does the Secretary select an application for funding?

Comment. One commenter questioned the authority of the Secretary to consider geographic distribution of the most highly rated applications as a final factor in selecting applications for funding, because the ECIA does not mention geographic location.

Response. No change has been made. Section 760.32 of the final regulations enables the Secretary to select for funding those projects that are best located to serve as resources for solving educational problems nationwide. Because the ECIA does not contain any selection criteria for the Secretary to consider in making awards, it is necessary for the Secretary to issue regulations establishing selection criteria to be used in making competitive awards under the statute. The Secretary has the authority and discretion to "issue regulations * * * relating to the discharge of duties specifically assigned to the Secretary under [the ECIA]." 20 U.S.C. 3871(a).

With respect to demonstration projects, for example, the potential impact of a project may be greatest in the area in closest proximity to the location of the project. Therefore, in order to ensure nationwide impact of a competition limited to, for example, demonstration projects related to a particular educational priority, the Secretary believes it is appropriate to base the final selection of applications for funding, in part, on the geographic location of the applicant in order to ensure a broad and equitable distribution of projects throughout the Nation.

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Environmental Protection Agency

Friday
October 26, 1984

Part VIII

**Environmental
Protection Agency**

40 CFR Part 136

**Guidelines Establishing Test Procedures
for the Analysis of Pollutants Under the
Clean Water Act; Final Rule and Interim
Final Rule and Proposed Rule**

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[FRL-2636-6]

Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final Rule and Interim Final Rule with Request for Comments.

SUMMARY: EPA is amending its *Guidelines Establishing Test Procedures for the Analysis of Pollutants*, as proposed on December 3, 1979. EPA is also reprinting existing test procedures for the convenience of readers. However, only those test procedures which are new or revised are being promulgated for purposes of judicial review. The purpose of this amendment is to establish:

- New test procedures (including quality control requirements) for the analysis of priority toxic organic pollutants;
- A new test procedure for the measure of carbonaceous biochemical oxygen demand (CBOD);
- A new test procedure based upon inductively coupled plasma optical emission spectroscopy for the analysis of most of the regulated trace metal pollutants; and,
- Mandatory container materials, preservations, and holding times for samples of the parameters covered by this regulation.

The quality control requirements establish control limits for acceptable analytical performance. However, the specific control limits in the test procedures for the priority toxic organic pollutants are being promulgated as an interim rule with a request for comments. Comments should be limited to the calculation of the numerical warning limits for the revised quality control sections.

In accordance with the Clean Water Act (CWA), these procedures will be required for filing applications for National Pollution Discharge Elimination System (NPDES) permits and for State certifications. These test procedures will also be used for compliance monitoring and to express pollutant quantities, characteristics, or properties in effluent limitations guidelines and standards and in pretreatment standards set forth at 40 CFR Parts 402 through 699 (unless otherwise specifically noted or defined in those parts).

DATES: In accordance with 40 CFR 100.01 (45 FR 26048), this regulation shall be considered issued for purposes of judicial review at 1:00 p.m. eastern time, November 9, 1984. These regulations shall become effective for all methods except CBOD₅ on January 24, 1985. The regulation relating to CBOD₅ [40 CFR § 136.3(a) Table IB, parameter 14] will be effective November 26, 1984. Comments on the interim final rule for specific control limits [40 CFR § 136.3(a) Table IC, footnote 7, and Table ID, footnote 7] will be accepted until December 26, 1984.

Under section 509(b)(1) of the Clean Water Act, judicial review of this regulation can be obtained only by filing a petition for review in the United States Court of Appeals within 90 days after these regulations are considered issued for purposes of judicial review (see *NRDC v. EPA*, 673 F.2d 402, D.C. Cir., 1982). Under Section 509(b)(2) of the Clean Water Act, the requirements of this regulation may not be challenged later in civil or criminal proceedings brought by EPA to enforce these requirements.

The information collection requirements contained in 40 CFR 136.3(e), has not been approved by the Office of Management and Budget (OMB) and is not effective until OMB approves it. The incorporation by reference of certain publications listed in the regulation is approved by the Director of the Federal Register as of January 24, 1985.

ADDRESSES: Comments on the calculation of control limits should be labelled as "Section 304(h): Control Limit Calculations" and submitted to: Dr. Robert B. Medz, Water and Waste Management Monitoring Research Division, Office of Research and Development (RD-680), U.S. Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460. Telephone Number: (202) 382-5788.

Most of the public record for this rulemaking will be available for inspection from 8:00 A.M. to 4:00 P.M. in EPA's Public Information Reference Unit, Room 2404 (rear of the EPA Library), 401 M Street, SW., Washington, D.C. 20460. The remainder of the record (primarily materials describing interlaboratory studies) will be available at the Environmental Monitoring and Support Laboratory at the Andrew W. Breidenbach Environmental Research Center, 26 West St. Clair Street, Cincinnati, Ohio 45268, from 8:00 a.m. to 4:00 p.m., Monday through Friday.

The EPA information regulation (40 CFR Part 2) allows the Agency to charge a reasonable fee for copying.

FOR FURTHER INFORMATION CONTACT: Dr. Robert B. Medz, at the address listed above or call (202) 382-5788.

SUPPLEMENTARY INFORMATION:

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I. Authority

Today's amendment was proposed on December 3, 1979 (44 FR 69464). It is being promulgated under the authority of sections 301, 304(h) and 501(a) of the CWA, 33 U.S.C. 1251 et seq. Section 301 forbids anyone to discharge any pollutant into navigable waters except pursuant to an NPDES permit issued under the CWA. Permits are issued under § 402, which is referenced in Section 304(h). Subsection 304(h) requires the Administrator to "promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to section 401 of the Act or permit application pursuant to section 402 of the Act." Section 501(a) authorizes the Administrator "to prescribe such regulations as are necessary to carry out his functions under the Act."

The Administrator has also made these test methods applicable to monitoring and reporting of NPDES permits (40 CFR Part 122, Subsections 122.21, 122.41, 122.44, and 123.25), and implementation of the pretreatment standards issued under section 307 of the CWA (40 CFR Part 403, Subsections 403.10, and 403.12).

II. History and Background

A. Structure and History of 40 CFR Part 136

The Administrator first approved test procedures for the analysis of wastewater pollutants on October 16, 1973, and first amended the list of approved test procedures on December 1, 1976 (See 38 FR 28758, October 16, 1973 and 41 FR 52780, December 1, 1976).

The full texts of the approved test procedures incorporated by reference in the regulation are considered to be part of the regulatory language. Most of the test procedures were cited from the following compilations of consensus test procedures:

- "EPA Manual of Methods for the Chemical Analysis of Water and Wastes,"
- "Standard Methods for the Examination of Water and Wastewater,"
- "American Society for Testing and Materials (ASTM) Annual Book of Standards, Part 31, Water,"
- "Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC),"
- "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments of the U.S. Geological Survey."

Additional test procedures were incorporated from other standards groups, such as the American National Standards Institute (ANSI), or from the open literature. Several test procedures, such as those for the analysis of benzidine, were incorporated from specific EPA sources.

Test procedures have previously been approved for about 115 different parameters. Those procedures apply to the analysis of inorganic (metal, non-metal, mineral), nutrient, demand, residue, radiological, organic, bacteriological, and physical parameters. For any given parameter, the regulations generally approved several different analytical methods. The December 1, 1976 amendments to 40 CFR Part 136 approved certain test procedures which were identified in tabular form (Table I). The discharge parameters to be measured were presented alphabetically. Each parameter was followed by a brief test

procedure description and by page numbers of the incorporated references. This unambiguously identified the approved test procedure.

An equivalency program is provided in 40 CFR Part 136. Under this program the Administrator may approve alternate test procedures developed and proposed by dischargers or other persons. If dischargers or other persons wish to use such alternate test procedures, they must apply to the State or Regional EPA permitting office (for limited approval) and to the Director of the Environmental Monitoring and Support Laboratory in Cincinnati (for nationwide approval). The equivalency provisions are included in these guidelines to encourage the development of new analytical methods, and to give analysts a number of options for resolving analytical problems that may be unique to specific wastewaters.

Finally, there may be discharges from some particular industries which need to be regulated on the basis of parameters or test procedures which have not been proposed and approved within the scope of the test procedures guidelines under 40 CFR Part 136. EPA may include such parameters and alternate test procedures within the rule-making for these industries in accordance with the provisions prescribed at 40 CFR 401.13, "Test Procedures for Measurements." Such test procedures may be integrated into the text of future amendments and revisions of 40 CFR Part 136.

The following provides a brief regulatory history of 40 CFR Part 136 prior to the current amendment.

- First proposal: 38 FR 17318 (at 40 CFR Part 130, later redesignated as Part 136), June 29, 1973.
 - First promulgation: 38 FR 28750 (at 40 CFR Part 136), October 16, 1973.
 - First amendment proposal: 40 FR 24535, June 9, 1975.
 - First amendment promulgation: 40 FR 52780, December 1, 1976.
 - Second amendment proposal: 44 FR 69464, December 3, 1979.
 - Correction Document, second amendment proposal: 44 FR 75031, December 18, 1979.
 - Comment period reopened, second amendment proposal: 46 FR 3033, January 13, 1981.
 - Equivalent Alternate Test Procedure Approvals:
- Chemical Oxygen Demand: 43 FR 9341, March 7, 1978.
- pH and Ammonia: 43 FR 38618, August 29, 1978.
- Nitrite Nitrogen: 44 FR 25505, May 1, 1979.
- Manganese: 44 FR 34193, June 14, 1979.

Chemical Oxygen Demand: 45 FR 26811, April 21, 1980.

Copper and Zinc: 45 FR 36166, May 29, 1980.

Iron: 45 FR 43459, June 27, 1980.

Residual Chlorine: 46 FR 58489, December 2, 1981.

Many reviewers of the proposed amendments requested that certain documents upon which the procedures were based be made available for review. In response, the Administrator sent 38 supporting documents to EPA's Regional Offices and to the EPA Headquarters Library in Washington, D.C., for inspection by the public. The closing date for comments was also extended from February 1, 1980, to April 28, 1980, to permit adequate time for public inspection of the record.

The Agency also started a series of formal inter-laboratory collaborative validation studies (each comprising of 15 to 20 laboratories) for the trace organic priority pollutant test procedures and the trace metal ICP test procedure. These were designed to establish expected inter-laboratory precision and accuracy characteristics of the test procedures.

Late in 1980, representatives of the Chemical Manufacturers Association (CMA), the American Petroleum Institute (API), and EPA met informally to discuss the reliability of some of the proposed test procedures. On January 5, 1981, these representatives met again to more formally discuss these concerns. CMA and API felt the test procedures for the toxic organic priority pollutants should not be promulgated as final until the inter-laboratory validation studies had been completed. The comment period was reopened on January 12, 1981, to allow all interested persons to inspect the official transcript of the January 5, 1981 meeting, and if needed, to amend their earlier comments on the proposed regulation. The extended comment period closed on February 2, 1981.

B. Consent Decree and the Priority Pollutants

In 1976, the Agency entered into a consent decree in the District Court of the District of Columbia (*Natural Resources Defense Council, Inc., et al. v. Train*, 8 ERC 2120 (D.D.C. 1976), as modified 12 ERC 1833 (D.D.C. 1979), and by the Court's Orders of October 26, 1982, August 2, 1983, January 6, 1984, and July 5, 1984), and the decree requires EPA to study the occurrence of 65 categories of pollutants in industrial wastewaters, and to limit the discharge of those pollutants in effluent by issuing effluent guidelines based on the "best

available control technology economically achievable" (BAT), pretreatment standards for new and existing sources, and new source performance standards. (Note: Within those 65 categories, 114 specific organic toxic pollutants and 15 inorganic pollutants were identified for a total of 129 specific toxic pollutants studied by EPA. Bis-chloromethyl ether (46 FR 10723, Feb. 4, 1981) and dichlorofluoromethane and trichlorofluoromethane (46 FR 46103, Jan. 8, 1981) have since been removed from the list, leaving 126 toxic pollutants now listed as "priority" toxic pollutants). The Agency began development of test procedures for measuring these pollutants in complex industrial wastewater matrices.

Paragraph 4(c) of the Consent Decree also required the EPA to establish and implement a program to identify and study pollutants other than the priority pollutants. At a minimum, EPA was to consider those additional pollutants listed in Appendix C of the Settlement Agreement. Those additional pollutants were not included in the December 3, 1979 proposal of the regulation. In studying Methods 1624 and 1625, EPA has evaluated applying the methods to those additional pollutants. A separate notice in today's *Federal Register* proposes to extend the scope of those methods to include the paragraph 4(c) pollutants.

The 1976 Test Procedures Guidelines (41 FR 56780, December 1, 1976), provided approved test procedures, selected from the various consensus standards, for 14 of the 15 inorganic priority toxic pollutants. The exception was asbestos, for which no adequate procedure was then available. The 1976 Guidelines also provided approved test procedures, similarly selected, for several chlorinated organic compounds (including PCBs, pesticides, benzidine, and pentachlorophenol). However, neither those procedures nor existing consensus standards were adequate to meet the testing requirements for all of the 114 priority toxic organic pollutants.

To fill this gap, the Agency embarked on an extensive program to develop additional test procedures to implement sections 301, 304(h) and 402. By 1979, these test procedures had been developed to a stage that represented the state-of-the-art analysis of the trace organic priority pollutants in industrial wastewater discharges. On December 3, 1979 the Agency proposed these methods, together with a test procedure for analysis of trace metals by inductively coupled plasma optical emission (ICP) and a test procedure for

determining the carbonaceous biochemical oxygen demand of municipal wastewaters, as amendments to 40 CFR Part 136.

III. Summary of the Proposed Regulation

A. Purposes

On December 3, 1979, the Agency proposed to revise the "Guidelines Establishing Test Procedures for the Analysis of Pollutants." The primary purposes of this proposal were:

- (1) To amend Table I, List of Approved Test Procedures, by adding the priority toxic organic pollutant parameters and approved alternate test procedures for their analysis;
- (2) To add an approved test procedure for a new parameter, "carbonaceous biochemical oxygen demand" (CBOD), which is important to secondary biological treatment technology for municipal wastewaters;
- (3) To approve an additional state-of-the-art test procedure based on the inductively coupled plasma optical emission (ICP) principle for the analysis of most of the trace metal parameters which were already covered in Table I; and,
- (4) To remove Table I, footnote 1, which recommended sample container materials, preservation procedures, and maximum holding times, and to specifically list those elements as mandatory requirements in a new Table II, "Required Containers, Preservation Techniques, and Holding Times."

Several test procedures were included for each of the priority toxic organic pollutants. This allowed several analytical options for most analyses. The CBOD parameter was included for analysis of a new specific measure of oxygen demand. The ICP test procedure was included to provide an additional and more rapid tool for trace metal analysis. Mandatory sample container materials, preservation techniques, and maximum holding times were included because these have been found to be critical to assure NPDES data quality.

The test procedures for the toxic organic priority pollutants were developed by the Agency in response to the mandates of the Consent Decree. At the time of proposal, the test procedures had been subjected to intensive single laboratory developmental testing. They were considered to be the best state-of-the-art test procedures available for the routine analysis of treated wastewaters for organic pollutants. They also appeared to be applicable to the analysis of untreated wastewaters. Multi-laboratory validations of these test procedures had been planned but had not yet been started. The Agency

decided to propose the test procedures for priority toxic organic pollutants before completion of the inter-laboratory validation studies because:

- Even without inter-laboratory validation these were (and are) the most tested and intensively validated test procedures available for the analysis of the toxic organic priority pollutants in industrial and municipal wastewater discharges,
- Many permits were expiring and permit renewals would require some provision for priority pollutant analysis,
- The new round of BAT effluent guidelines regulations would include limits on priority toxic organic pollutant discharges, and,
- The priority toxic organic pollutants would need to be reported under the permits regulations at 40 CFR Parts 122 and 123, and by pretreatment regulations at 40 CFR Part 403.

The following discussion covers the provisions of the proposed regulation in more detail.

B. GC, HPLC, and GC/MS Test Procedures

Since 1976 the text of the regulation has listed pollutant parameters alphabetically in Table I, "List of Approved Test Procedures,"—either as specific compounds or entities such as "Benzidine" or as classes of compounds or entities such as "Pesticides." The individual parameters within such classes, when identified, were entered alphabetically within the class. Approved test procedures were then identified by test procedure descriptors and by page numbers in specifically identified references. In the case of "Pesticides" and several other organic chemical classes, the Table refers to the full text of the approved test procedures in order to clearly identify the scope of the test procedures.

In 1979 the Agency proposed to consolidate all of these organic chemical parameters under a new class entry, "Organic Compounds", and to identify alphabetically all of the specific organic compounds which were included within the scope of the various approved test procedures. All of the test procedures and organic compounds which were approved in 1976 continued to be approved, and were re-printed (unmodified) in the proposal only because Table I was being restructured.

The new organic chemical entries in Table I were the 114 (now 111) priority toxic organic pollutants and the proposed test procedures for their analysis. Twelve of the proposed test procedures were based on gas chromatography (GC) and/or high-

pressure liquid chromatography (HPLC). Three of the proposed alternate test procedures were based on gas chromatography with mass spectrometric detection (GC/MS).

Chromatography is the technique by which compounds in mixtures are separated by interaction between a mobile and a stationary phase. The stationary phase is placed in a tube called a column, and the mixture is moved through the column by the mobile phase under the influence of a pressure differential across the tube. Different compounds are carried through the column at different speeds by the mobile phase. The order in which the compounds exit the column (elute) is determined by the chemical and physical properties of the compounds and of the mobile and stationary phases. In each method the stationary and mobile phases are selected to give the most effective separation of the compounds of interest.

In gas chromatography (GC), the mobile phase is a gas, and the stationary phase is usually a high molecular weight liquid, coated on an inert support or on the column wall of a very small diameter tube (an open tubular column). In liquid chromatography (LC) the mobile phase is as solvent, and the stationary phase is usually a selective adsorbent. As compounds in the mixture elute (exit) from the column, their presence is indicated by various detectors. One detector is the mass spectrometer, hence the term GC/MS. Following detection, the compounds can be identified and then quantified by a computer or by the analyst.

Separations by chromatographic techniques are not always complete. Several compounds within a mixture which have similar chemical and/or physical properties may simultaneously elute from the column, along with the compounds of interest. These are known as interfering compounds or interferences.

Where compounds are easily identified, conventional detectors can often make better quantitative assessments than GC/MS can. However, in many cases, the conventional detectors used in chromatography are not able to discriminate between the compounds of interest and the interferences. In such instances, a mass spectrometer usually is able to discriminate between the compounds of interest and the interferences. Thus, it would be the preferred detection system where interferences are expected or many compounds must be identified. An alternative solution is to use a second column containing a different stationary phase. This aids in the identification of

the compounds of interest by providing additional qualitative identification when conventional chromatography detectors are used.

The low cost of the conventional GC detectors, relative to MS, makes the GC option particularly attractive for routine monitoring of small numbers of pollutants. On the other hand, the GC/MS test procedures allow for the simultaneous or rapid sequential measurement of large numbers of different organic pollutants. They also provide certain structural information that can be used to minimize interferences that would mask compound identification by the less specific conventional GC detectors.

EPA divided priority toxic organic pollutants into 12 categories, based on their physical and chemical properties and chemical structures. A GC or HPLC test procedure was then developed for each category, with the expectation that the pollutants within each category could be measured by a single procedure. These procedures were to be routinely used where the pollutants to be measured were known to have a high probability of occurrence. GC and HPLC could also be used for qualitative identifications of unknown materials, although the proposed GC/MS test procedures were more suitable for this purpose. In most cases, several GC or HPLC configurations of inlet, column, operating conditions, and detectors were recommended with each procedure. Each test procedure stipulated that, if it were used to screen samples for priority pollutants, an analyst needed to verify any compound identified with an independent analytical protocol. The GC/MS was suggested as such a protocol.

In the proposed tests of the organic toxic priority pollutant test procedures, it was not EPA's intent to require separate samples for each test procedure. Subsequent comments have indicated that this was not clear from the test procedure texts or in the proposed sample preservation and holding time requirements in Table II.

C. Quality Control and Quality Assurance

Quality control (QC) includes all of the means taken by an analyst or an analytical laboratory to make certain that the total measurement system, including the analyst's performance and matrix problems, are calibrated correctly or accounted for, and remain in calibration or accounted for in all ensuing analyses. Quality assurance (QA) includes all the means taken within or beyond the laboratory to make certain that the measurement systems in

different laboratories in a monitoring network remain in calibration with a common external standard, and hence with each other. QA/QC seeks to assure that analyses of the same substances taken by different analysts at different times and places are of the same quality and are comparable within known statistical confidence limits. EPA proposed that the QC within the GC and HPLC test procedures require the use of field replicates to validate the precision of sampling techniques. Laboratory replicates and fortified samples were also proposed in 1979 to validate the precision and accuracy of analyses. Since EPA's studies in this area were not yet finalized at the time of the proposal, additional quality control guidance was described in general terms and proposed as necessary to enable evaluation of the performance of test procedures.

Similar GC configuration and quality control guidance was proposed for the GC/MS test procedures, except that the GC/MS could be used in a screening application without a mandatory confirmation protocol. However, a separate, more intensive quality control procedure was proposed and described in detail, as it might be applicable to the GC/MS test procedures.

D. Other Table I Organic Parameters

Proposed Table I was restructured to include the previously designated organic parameters benzidine, pentachlorophenol, Aldrin, δ -EHC, γ -BHC, chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan, Endrin, and Heptachlor as specific entries in the organic compounds subsection. The previously approved test procedures (41 FR 52780, Dec. 1, 1976) for most of the organic pollutants incorporated within Table I had been entered without changes under the broad parameters "chlorinated organic compounds (except pesticides)" and "pesticides." These broad parameters included test procedures for chlorinated organic solvents, chlorinated hydrocarbon pesticides, carbamate pesticides, triazine pesticides, phosphate pesticides, and chlorinated phenoxy carboxylic acid pesticides. Approved test procedures for these parameters have been available on request from EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio (EMSL-CI).

E. ICP Test Procedure (ICP)

The ICP test procedure was proposed as an additional option for the analysis of 23 trace elements: aluminum, arsenic, barium, beryllium, boron, cadmium,

calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silicon, silver, sodium, vanadium, and zinc. It was listed in Table I, under Metals. Lithium and strontium were also included within the scope of the ICP method although the consent decree had not listed them as high priority toxic parameters. This proposal did not affect the previously approved atomic absorption (AA), voltametric, gravimetric, flame photometric, and colorimetric test procedures referenced in Table I for these elements.

The ICP test is a rapid, multielement procedure, representing state-of-the-art. It was proposed because of its time- and cost-effectiveness, and because available data showed it to be equivalent to the other approved procedures for analyzing the designated metals in wastewater discharges.

F. CBOD₅ Test Procedure

The CBOD₅ test procedure was a new parameter proposed in Table I. It responded to many requests for an approved procedure to measure the carbonaceous component of oxygen demand. It was a draft version of the consensus method now included as Method 507 paragraph e(6) in the 15th Edition of "Standard Methods for the Analysis of Water and Wastewater."

The CBOD₅ is a different measure of oxygen demand than the total BOD₅ (Standard Method 507). Thus it cannot be used to analyze oxygen demand when an NPDES permit calls for BOD₅ to be measured. The CBOD₅ procedure uses a nitrogen biochemical oxygen demand inhibitor. This inhibitor allows oxygen to be consumed only by organisms that require carbon as their nutrient source. In the presence of such an inhibitor, the nitrogen compounds remain refractory to biochemical degradation, since the activity of nitrifying organisms is suppressed.

IV. Highlights of Final Test Procedures

A. Restructuring of Table I

Users familiar with the former text of section 136 will first notice the reorganization of Table I, which lists pollutant parameters for which approved analytical methods exist, and indicates the approved method(s) available for each parameter. In the 1976 regulations, the parameters in Table I of § 136.3(a) were organized around broad categories, such as bacteriological test procedures and test procedures for metallic or residue parameters. These broader categories were then entered alphabetically into Table I.

Analyses for an additional 111 organic parameters have now become essential. However, entering all those parameters into a single list of approved methods became unwieldy, especially with the proliferation of footnotes to the table. Therefore, to make Table I easier to use, it has been restructured for this final rulemaking into five sub-tables:

- Table IA. List of Approved Biological Test Procedures.
- Table IB. List of Approved Inorganic Test Procedures.
- Table IC. List of Approved Test Procedures for Non-Pesticide Organic Compounds.
- Table ID. List of Approved Test Procedures for Pesticides.
- Table IE. List of Approved Radiological Test Procedures.

Throughout Table I, EPA has updated numerous references to consensus methods, e.g., from the 14th to the 15th edition of "Standard Methods." These changes are technical amendments without substantive effect and are promulgated as final amendments. EPA has determined that notice and public procedure on these updates are unnecessary and contrary to public interest. See 5 U.S.C. 553(b)(3)(B).

These technical amendments should not affect any on-going enforcement actions or other regulatory actions on analyses performed with earlier methods. Today's amendments do not approve consensus methods adopted since the proposal when they contain substantive revisions to the previously approved methods. Instead, the Agency has retained its approval of the prior method. Examples discussed below include the retained approval of the 14th edition Standard Method for phenols (4AAP), and the limited approval of the U.S.G.S. method for fecal streptococci which, as approved, is identical to the previous U.S.G.S. method.

Table IA includes bacteriological test parameters which were approved in the 1976 Guidelines. Approved methods for their analysis are now listed in a new format; they are not substantively changed. Previously cited references have been updated. With the exception of the U.S.G.S. test procedures for fecal streptococci, no changes have been made in the test procedures. As noted only editorial changes have been made in the texts of the other test procedures in these updated references.

A new EPA reference is now approved for several bacteriological test parameters. The updated USGS fecal streptococci test procedure is approved only if the dissolution of the nutrient medium is conducted in a boiling water bath. This is because dissolution on a hot plate or over an open flame (which

appears to be permitted in the updated reference) can lead to scorching or to other alterations in the nutrient medium.

Table IB includes all of the inorganic and physical parameters that were in the 1976 Guidelines. The previously cited references have been updated.

The ICP test procedure is now approved as an additional alternate test procedure for the analysis of 25 Table IB trace element parameters. Antimony and thallium are now included within the scope of the ICP test procedure in response to information made available in comments which were received. The only new parameter which has been added to Table IB is the Carbonaceous Biochemical Oxygen Demand (CBOD₅) parameter.

Table IC includes 97 organic, non-pesticide chemical parameters. Test procedures for 21 of these parameters were approved in the 1976 Guidelines and continue to be approved, unchanged, in Table IC. Ninety-five of the Table IC parameters (including 19 parameters approved since 1976) are priority toxic organic pollutants for which new test procedures were proposed. The new test procedures are essentially the same as those proposed, with the exception that, (1) where possible, they have been made more flexible in response to comments and (2) quality assurance and quality control standards have been defined. Two newly-modified GC/MS test procedures, Methods 1624 and 1625, which are variants of Methods 624 and 625, have been added to Table IC. They differ from Methods 624 and 625 by utilizing stable, isotopically labeled analogs of the analytes as internal standards for GC/MS analysis. This allows the analyst to accurately correct for variability in analyte recovery efficiency, responding to a criticism raised by commenters.

With the exception of the test procedures for benzyl chloride and epichlorohydrin, all test procedures in Table IC prescribe quality control limits. The actual specific control limits are the sole elements of this regulation which are promulgated as an "interim final" action. This is because the data base and calculations of these limits have been developed since proposal. However, the idea of specific mandatory, acceptability criteria was fully proposed, favorably commented on, and finally accepted. Thus the regulatory framework for the specific limits is being promulgated as final.

Table ID contains the 67 parameters included under the general "pesticides" parameter in the 1976 Guidelines. Although most pesticides are organic

compounds, they have been listed separately in Table ID rather than with the other organic parameters in Table IC because of the wide association between this subset of organic compounds and their end use. Sixteen of the 67 parameters are priority pollutants. Three additional pesticides were identified as priority pollutants under the consent decree. Table ID therefore now identifies 70 specific pesticides, of which 19 are priority pollutants. Methods 608 and 625, which were proposed for the priority organic toxic pollutants, were revised to incorporate substantive comments. All other references in Table ID have been updated, but the updated references do not require any substantive changes from previously approved test procedures.

Table IE now includes the five radiological test procedures approved in the 1976 Guidelines. All references have been updated, and an EPA reference has been added. There are no substantive textual changes in these updated test procedures.

B. GC, HPLC, and GC/MS Test Procedures

Analyses for organics depend upon a variety of chromatographic techniques. See subsection III-B above. EPA proposed and is approving two HPLC methods (605 and 610), 10 GC methods, and three GC/MS methods (613, 624, and 625). In addition, EPA has responded to critiques of Methods 624 and 625 by approving two GC/MS/isotope dilution variants (1624 and 1625). Each method is accompanied by a specific set of quality assurance (QA) procedures. The QA process relies on specific control limits calculated for each parameter for which the method can be used. The control limits indicate the outer range of precision and accuracy found in an extensive inter-laboratory study. The limits represent the minimum threshold of quality expected of competent laboratories: 95 percent confidence level per compound for the 600 series and the 99 percent confidence level across the set of compounds for the 1624 and 1625 methods. Most analyses should have far better precision and accuracy. The calculations of specific numerical control limits for the calibration and quality control sections of the GC, HPLC, and GC/MS test procedures is interim final. This means that they are legally effective, but that EPA will accept comments on their calculation. All other parts of these test procedures are finally approved for the analysis of the parameters which are indicated in Table IC and ID.

Each method is approved for specific organic compounds. In general, GC Methods 601-603 and GC/MS Methods 624 and 1624 are approved for the analyses of the purgeable priority pollutants. GC Methods 604 and 606-612 and GC/MS Methods 625 and 1625 are approved for the analysis of the non-purgeable, volatile priority pollutants, including, for Method 625 only, the priority pesticide pollutants. Method 625 is also approved for screening samples for 2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzo-p-dioxin), but only GC/MS Method 613 is approved for final qualitative confirmation or quantification of 2,3,7,8-TCDD in samples. HPLC Methods 605 and 610 are also approved for the analysis of the nonpurgeable volatiles (the benzidines and polynuclear aromatic hydrocarbons). Methods 1624 and 1625 are approved for use interchangeably with the other test procedures which are being approved for the analysis of the priority toxic organic pollutants. Their most significant difference from Methods 624 and 625 is the requirement that, where available, stable, isotopically-labeled analogs of the priority pollutants are to be used as method internal standards. Since Methods 624 and 625 do permit flexibility in the selection of internal calibration standards and surrogate standards, Methods 1624 and 1625 are, in essence, acceptable variants permitted by Methods 624 and 625. They improve on Methods 624 and 625 and are generally preferable. However, Methods 624 and 625 are also being approved because they are widely available, slightly less expensive, and they are of use when interference and recovery efficiency are not expected to be problems.

In general, both GC/MS and non-MS test procedures have been approved for each of the priority toxic pollutants. Most of the revisions of the proposed test procedures were made either for clarification or to give the analyst more flexibility to practice professional judgment. These procedures now contain a section on safety, cautioning analysts of the potential hazards associated with exposure to the chemical reagents required by the test procedures, or to the toxic chemicals being analyzed. Recommended and mandatory quality assurance practices are also given in each of the test procedures.

Methods 601-604, 606-609, 611-613, 624, 625, 1624, and 1625 include specifications for performing the tests. These specifications are based on a required primary GC column and

specified detector. A primary HPLC column and specified detector are required for Methods 605 and 610 and specifications are provided. The primary column is also used to identify the pollutant. A secondary column and detector are also defined, but not required, for non-MS Methods 601-604 and 606-611. The secondary column and detector can be used for confirmation of priority pollutants identified by the primary column for unfamiliar (non-routine) samples (see sections 1.2 of the methods). The GC/MS test procedures are suggested as the confirmatory test for identifications made by Methods 605 and 612, and may also be used as the confirmatory test for identifications made by Methods 601-604 and 606-611. For example, an unfamiliar sample which would be likely to need confirmation would be a single sample taken for an NPDES application. See 40 CFR 122.21. In contrast, routine monitoring, such as that for discharge monitoring reports, would be less likely to require a secondary column for confirmation since the sample is more likely to be familiar to the analyst.

Methods 606, 609, 611 and 612 all use essentially the same procedure for sampling, sample extraction, and concentration. Thus a single sample may be used to measure the parameters within the scope of these methods.

Sample container materials, preservation techniques, and holding times are critical to the procedures and are specifically defined (Methods 601-613, 624, 625, 1624 and 1625). The design and operation of the purge-and-trap device in Methods 601-603, 624 and 1624, and the sample extraction procedures of Methods 604-613, 625 and 1625 are precisely defined as well.

In response to public comments, substantive revisions were made to allow more flexibility in the remaining parts of Methods 601-613, 624, 625, 1624 and 1625. In Methods 604-613, after the sample has been extracted, the analysts are now free to choose a technique to concentrate the extract. The same flexibility is provided for selecting the GC or HPLC configurations (column packings, operating conditions, and detectors). When analysts use concentration techniques or chromatographic configurations other than those described in the test procedures, their approaches must meet the performance criteria defined in the section of the procedures dealing with calibration and quality control.

The most difficult task in finalizing the methods for organic analyses was defining the relationship between desirable flexibility in the methods and

necessary quality control. The proposal specifically solicited comments on both issues and many comments were received on each. The final methods resolve the issue by allowing far greater method flexibility, but by establishing specific control limits as a mandatory part of the quality control procedure.

The proposal noted, and comments confirmed, that method flexibility should be inherent in the methods. Historically, rigid protocols have been a problem in organics analyses. For example, an analyst may be using a method, other than mass spectrometry, to identify a few specific components out of the several million known to exist. This requires that interferences be overcome and "canned" approaches may not effectively address interferences, particularly where matrices are variable or diverse. Thus, the Food and Drug Administration (FDA) and AOAC and other method standardization organizations have usually provided optional "clean-up" procedures for organics, for example, permitting analysts to use Florisil clean-up for pesticides. Further, the analyst may be interested in measuring only a few compounds, while the proposed method may be designed to measure large categories of compounds. For example, a particular industry may be regulated only for the compound that elutes from the gas chromatography after a long program temperature run. An inflexible method might require the analyst to go through the entire temperature run to look for a single peak that elutes late in the chromatogram. This may be needlessly inefficient. For such reasons, EPA has decided to permit flexibility in chromatographic conditions.

Commentors also raised concerns about inflexibility in sample preparation. They objected to the Kuderna-Danish glassware concentration technique being the only approved approach for concentrating extracts. In fact, if the analysts are measuring only the less volatile compounds in a method category, it may not be necessary to require a rigid procedure for concentration. In this case, it may be appropriate to allow other procedures for concentrating extracts.

After considering these issues, the Agency has decided to allow limited flexibility within the methods. Specifically, chromatographic conditions, including column packings and detectors can be varied. This approach allows continued technical development of the methods. Thus EPA avoided a rigid prescription of

technology that would soon be obsolete due to the rapid advances occurring in chromatography. However, the primary objective underlying this flexibility is to enhance precision and accuracy for each analysis. Flexibility should not be permitted if the altered technique would be less precise or less accurate than the standard approved analytical method. Thus, a corollary of increased flexibility was an increased need for a rigorous and unambiguous quality control procedure.

These basic decisions had become clear by the time of the second, reopened comment period. The comments received in the second comment period again supported the issue of quality control and requested that the criteria be specified more clearly. Another general comment was that the criteria should wait for the results of the inter-laboratory method validation studies and be based upon those results. Today's rulemaking reflects these comments, while specifying that EPA will accept further comments, limited specifically to the calculation of control limits from that new data base.

The quality control procedures now take two different forms. First, there is a "start-up test" to establish the laboratory's basic ability to set up and operate the analytical equipment and procedure. The purpose of the start-up test is two-fold; it establishes that analytical equipment has been properly set up, and it demonstrates the basic ability of the analyst to recognize the compounds of interest. It is required every time the method is changed. It requires the analysis of four spiked distilled water samples. The analyst compares his measures of precision and accuracy to establish criteria developed from the inter-laboratory method validation studies. Because of the basic threshold nature of the start-up test, the methods allow the test to be performed with reagent water.

If the analyst fails the criteria for accuracy or precision in the start-up test, the analyst is to repeat the test for any compound that fails a criterion. If the analyst is measuring, for example, eight compounds at once using Method 601, and fails the criteria for three of them, the analyst is required only to repeat the three that failed provided the method is not changed. It is not very difficult to meet the criteria for any individual compound. However, when one is analyzing for numerous compounds there is an accumulation of failure probabilities; that is, an increased likelihood that one of several parameters will fail for "statistical"

reasons. Thus EPA allows a "second pass" opportunity to meet the criteria, as long as the method is not changed. Exhibit 1, below, offers some guidance as to when analysts may want to skip the "second pass" opportunity based on an excessive number of test criteria failures occurring on the first pass. An excessive number of failures should not occur if the system is operating properly. Thus, such a number of failed criteria may suggest poor operation to the analyst. In this case, the first pass criteria failures suggested the compound(s) tested would fail a second round. The analyst may wish to simply adjust the system and reinitiate the start-up test.

If the method is changed as a result of the initial test, the startup begins again. For example, if the start-up test indicates zero recovery of vinyl chloride and a check reveals that the instrument trap was installed backwards, the operator must correct the problem and reinitiate the test for all compounds, since the method was just modified.

The second form of quality control is contained in the ongoing quality control program. Laboratories are required to analyze blank samples (e.g., reagent water) daily, and to analyze spiked wastewater samples periodically. Ten percent of all samples are to be spiked (five percent for Methods 624 and 625). The resulting accuracy of recovery must be compared to the established accuracy criteria for the method developed from the results of the inter-laboratory method studies.

If an analyst fails one or more accuracy criteria with the spiked wastewater, the analyst must analyze a check sample (e.g., spiked reagent water). The purpose of analyzing the check sample is to establish whether the inaccuracy is caused by matrix effects or by the laboratory operating improperly (i.e., out of control). Again, accuracy results are compared to the established accuracy criteria. The criteria for acceptable accuracy in these methods are based upon accuracy derived from testing reagent water. Use of check samples rather than spiked wastewater to verify the accuracy criteria for a laboratory is consistent with the fact that one set of regression equations in the inter-laboratory method study is derived from reagent water. That set of regression equations is the basis quality control criteria.

The decision to rely on spiked wastewater samples for the initial test is an alternative to requiring that analyses be conducted on ten percent spiked reagent water samples (to verify laboratory control) and ten percent of

spiked wastewater samples (to verify matrix effects). Accordingly, the need to also analyze a check sample is reduced to a second-tier requirement which is only mandated if accuracy criteria are not met with spiked wastewater.

The limits that are in the methods have been derived on a compound-by-compound and method-by-method basis. They are derived directly from the inter-laboratory method validation studies. The formal inter-laboratory validation studies for Methods 601-602, 604-613, 624, 625, and 1625 have been completed with 15 to 20 laboratories. These fifteen methods have been revised to include methods performance results derived from these studies.

Two methods (603 and 1624) have not been subject to an inter-laboratory validation study. A formal inter-laboratory validation study for Method 603 has not been completed due to an error in the draft method. Although the error was corrected, EPA was not able to perform an inter-laboratory validation study on the same scale as performed for the other methods. However, one commercial laboratory did validate the method and that validation was verified by EPA's laboratory. In addition, the method is similar to Methods 601 and 602 and the results from the validation are similar. EPA believes that the validation of 603 is adequate to establish that the method is appropriate. Therefore, Method 603 is being promulgated with warning limits based upon the best data now available.

Method 1624 was not formally validated through an inter-laboratory study. The specifications for Method 1624 were developed from Method 624 which was formally validated. In informal multi-laboratory and single-laboratory studies, Method 1624 has been shown to yield slightly better performance on treated effluents than Method 624, but this improvement is insufficient to warrant a separate inter-laboratory validation study.

The multi-laboratory validation studies were designed according to the method of W.J. Youden (Youden, W.J., "Statistical Technique for Collaborative Tests," Statistical Manual of the Association of Official Analytical Chemists, 1975) in which pairs of samples having slightly different spiked concentrations of the compound of interest are analyzed. Each collaborating analyst analyzes a sample only once and reports a single value. By having the analyst perform the analysis as he would have done for a normal routine sample, the Youden design helps to avoid accidental manipulation of data that can sometimes occur in a

laboratory doing replicate determinations.

Each Youden sample pair for a given parameter is prepared so that the concentration of the pollutant of interest in one-half of the pair is similar to, but measurably different from, the concentration of the pollutant in the other half. Three Youden pairs were analyzed for each of the parameters. The mean values of each of the three pairs were designed to spread over a usable and realistic range of concentrations. The lowest concentration pair was prepared so that the concentration would be above the minimum detection concentration for the method.

The Youden pairs, prepared as concentrates, were spiked into six different water matrices: distilled water, municipal drinking water, a surface water vulnerable to synthetic chemical contaminants, and usually, three different industrial wastewaters from industries that normally would be regulated for the priority pollutants under study. The data were reduced to four statistical relationships related to the overall study: (1) Multi-laboratory mean recovery for each sample, (2) accuracy expressed as relative error or bias (the difference between the multi-laboratory mean recovery and the true value divided by the true value), (3) the multi-laboratory standard deviation of the spike recovery for each sample, and (4) the multi-laboratory relative standard deviation. In addition, two statistics were reduced from the raw data relating to the single-analyst performance: (1) Single-analyst standard deviation, and (2) single-analyst relative standard deviation.

The single-analyst standard deviations were calculated for each of the sample pairs according to the method of Youden by (1) calculating the difference for recoveries from each sample pair reported by each analyst, (2) calculating the average value of these differences across the entire study, (3) calculating a "sum-of-the-squares" by adding the square of the differences between each difference and mean difference, (4) dividing the "sum-of-the-squares" by the degrees of freedom to give the single-analyst variance, and (5) taking the square root of the variance to give the single-analyst standard deviation.

Fifteen to twenty-five percent of the data generated in the multi-laboratory validation studies were discarded as outliers, i.e., data too far from the vast majority of data to be acceptable. Outliers were determined based on

widely accepted statistical tests prescribed by ASTM and AOAC.

There is an apparent linear relationship between the mean recovered spike values and the true spike values, overall standard deviation, and single-analyst standard deviation. These linear relationships have been expressed as regression equations over the concentration ranges studied in each matrix. Six different regression equations are derived for each of the six matrices for any given compound. In most cases the variations of the six lines do not appear to be statistically significant at the 5% significance level. The conclusions were reached for each water type by using the F-distribution to compare variance statistics of waste waters with those of distilled water. Mean recoveries were compared between wastewater and distilled water using paired t-test statistics.

EPA is aware that there are limits to the strength of these analyses. These comparisons assume independence among the observations and this was not exactly the case since the "spike" was made up of mixtures of all of the compounds under consideration in each method and hence there was an interdependence among compounds. Despite these limitations, the tests still provide strong evidence that water type generally had no statistically significant effect on the method's performance.

The multi-laboratory tests support an important conclusion. If a laboratory performs well with the methods using distilled water, it should be able to obtain good results with surface waters and industrial wastewaters. Based upon this conclusion, the multi-laboratory regression equations for accuracy and single-analyst overall precision for distilled or reagent water have been incorporated into the quality assurance and quality control provisions of the final texts of Methods 601, 602, 604-613, 624, and 625 to define method performance. The regression equations for the other matrices are also included in the texts of the methods.

The multi-laboratory validation of Method 1625 was performed at a single concentration in a reagent water matrix. Specifications were derived for linearity of calibration, for calibration verification, for retention time precision, for compound recovery from a reagent water matrix, and for precision and accuracy of analysis by isotope dilution and internal standard techniques. All specifications derived from the study are applied at the same level at which they were tested, and sample matrices which show labeled compound recoveries significantly different from

recoveries of these compounds from reagent water are diluted with reagent water to bring these recoveries into the expected range.

It is also important to note that the studies provide a strong basis for setting control limits which represent a range of acceptability. The studies show that most laboratories will do far better, especially on a single-operator, single-laboratory basis. Other performance studies, completed since the inter-laboratory analyses, incorporate too much flexibility to be directly analogous to EPA's collaborative test of the methods. However, they appear to confirm the assumption that most laboratories will exceed the minimum standards and indicate that method variability will be well within the range of the control limits.

The final specifications derived for all of the organics methods (except 603) were the result of a statistical analysis of the data from the multi-laboratory studies. These specifications adopt initial precision and accuracy for all methods. For start-up calibration verification, they specify control limits for Methods 601, 602, 624, 1624, 625 and 1625. For on-going accuracy, they specify control limits for recovery of pollutant spikes for Methods 601-613, 624, and 625, and for recovery of labeled compound spikes for Methods 1624 and 1625. The methods allow for simultaneous testing of all the parameters listed in each method.

In theory, a problem could arise from simultaneous tests for numerous compounds. The control limits have been calculated to allow only a 5% likelihood that a result that exceeds the limits for each compound is merely a statistical fluctuation (rather than actual error). However, the chance of "statistical error" rises with the number of compounds being tested.

EPA has corrected for this possibility in several ways. First, most users will not apply each analysis to all parameters simultaneously; thus they will have a greater chance of passing all test criteria. Second, in order to allow for simultaneous testing of all parameters in a given method, the specifications for accuracy and precision have either been broadened, or a re-test has been allowed, or both. The technique of using a re-test was chosen because a one-test-only specification which allowed for simultaneous testing of a large number of parameters would be so broad as to have little meaning. The provision for a re-test preserved a meaningful specification while allowing for simultaneous testing of all parameters. If a laboratory fails the re-test as well as

the initial test, the likelihood of "statistical error" is extremely low (5% times 5%, i.e., .0025 for a given compound). Third, when a re-test is required, it need only be performed on the particular compounds which failed the initial test. Finally, the control criteria for Methods 1624 and 1625—those most likely to be simultaneously used on many compounds—were determined based on the 99% confidence level.

As a voluntary guide to laboratories practicing a given method, the following Exhibit 1 gives suggested numbers of first pass test criteria failures which are unlikely if the laboratory is satisfying the probability based quality control specifications. It assumes all parameters in a given method are tested simultaneously. The Exhibit indicates the maximum number of parameters for which each method can be used simultaneously. The two right-hand columns indicate a certain number of unacceptable results. If the analyst finds that number, or a greater number, of unacceptable results, he may conclude that the entire analysis is flawed. If so, it may be more efficient to repeat the entire analysis than to re-examine only the compounds which exceed the control limits.

EXHIBIT 1.—SUGGESTED MAXIMUM NUMBER OF TEST CRITERIA FAILURES WHICH JUSTIFY REPEATING ENTIRE ANALYSIS

Method	Number of simultaneous parameters	Number of test startup ¹	Criteria failures on-going ²
601	29	7	4
602	7	3	2
603/605	2	2	2
604	11	4	3
606	6	3	2
607	3	2	2
608	25	6	4
609	4	3	2
610	16	5	3
611	5	3	2
612	9	4	3
613	1	2	1
624	31	7	5
625	61	11	7
1624	66	12	7
1625	151	7	5

¹ Based on twice the number of parameters being tested since both accuracy and precision are being evaluated.

² Based on the number of parameters being tested.

Section 8 of each method defines acceptable analytical performance limits for the GC, HPLC, and GC/MS test procedures (Methods 601-613, 624, 625, 1624, and 1625). These acceptable performance limits are also specified in Footnote 7 to Table IC, "List of Approved Test Procedures for Non-Pesticide Organic Compounds," and Footnote 7 to Table ID, "List of Approved Test Procedures for Pesticides." System performance is

acceptable only when the average recoveries and standard deviations of spikes of the pollutants of interest into reagent water meet these performance standards. Where large numbers of parameters are being analyzed (see Exhibit 1 above), there is an increased chance that at least one parameter will fail for either average recovery or standard deviation limits based purely on chance. Where such failure occurs, the spiking and recoveries must be repeated, but only for the failed parameters. Repeated failure confirms a general problem with the analytical measurement system. When such failed recoveries are experienced the system is judged to be out-of-control for the failed parameter. Thus, the results for the failed parameters in unspiked samples are suspect and cannot be reported to show regulatory compliance.

The acceptance criteria for spikes into samples for each parameter were calculated to include both an allowance for error in prior measurement of the background and another allowance for error in prior measurement of spike concentrations. The calculation assumed a spike-to-background ratio of 5 to 1. Thus such error will be accounted for to the extent the analysts' spike-to-background ratio approaches 5 to 1. In many cases this allows analysts a greater margin of error than should actually be expected. This is because the calculation assumes that two prior errors are cumulative, ignoring the degree to which they actually cancel each other out.

Today's final test procedures represent an effort to provide the maximum uniformity that is practical for a wide cross-section of classes of chemical compounds. They will be continually reevaluated for their general applicability to complex wastewater matrices.

The substantive revisions made in the GC, HPLC, and GC/MS methods in response to comments are discussed in the public participation section of this preamble. Three of the most significant changes include: (1) Addition of a confirmatory column to Method 602; (2) deletion (from 613) of the gas chromatographic/electron capture (GC/EC) test procedure for screening for 2,3,7,8-TCDD, and (3) revision of Methods 613 and 625 to show that Method 625 may be used whenever screening for 2,3,7,8-TCDD is required. The full text of the approved GC, HPLC, and GC/MS test procedures are being printed in Appendix A of this regulation.

The GC, HPLC, and GC/MS test procedures are now cited in the regulations in the new Table IC, "List of

Approved Test Procedures for Non-Pesticide Organic Compounds," and Table ID, "List of Approved Test Procedures for Pesticides."

C. ICP Test Procedure

The ICP test procedure is cited in the regulation as an additional analytical option for trace metal analysis in the new Table IB, "List of Approved Inorganic Test Procedures."

The ICP test procedure, Method 200.7, has been changed only slightly from the version proposed on December 3, 1979. EPA proposed that lithium and strontium be analyzed using the ICP test procedure, since these parameters could be analyzed using this method. Because EPA did not propose or develop accuracy or precision criteria for these parameters, EPA is unable to approve the ICP test procedure for them. EPA is considering the ICP and other alternative test procedures in a separate rulemaking. In light of additional information received in the public comments showing good recoveries for antimony and adequate recoveries for thallium by the proposed test procedure, both of these metals have been added to the scope of the ICP test procedure. Also in response to public comments the detection limit for silica has been doubled and the wavelengths of the metal are now given to the third decimal. In section 3 of the ICP test procedure a new definition for "Quality Control Sample" has been provided for clarification, and a new section on safety has been added to alert the analyst to the hazards of the toxic reagents and pollutants involved. Other revisions made in response to comments are discussed in the public participation section of this preamble. The full text of

the ICP procedure is printed as Appendix C to this regulation.

D. CBOD₅ Test Procedure

The final test procedure for CBOD₅ is essentially the same as that proposed. See Section III-D, above. EPA's proposed test procedure was taken from a draft *Standard Methods* test procedure for CBOD₅.

The final method language is the same as the language now included in the 15th edition of *Standard Methods*. This has required minor changes from the wording of the proposal, but no substantive changes were required.

E. Table II: Required Containers, Preservation Techniques, and Holding Times

Table II in Section 136.3(e) now restricts the materials of which sample containers can be made, and specifies the procedures by which samples are to be preserved. Table II also limits the maximum time for which samples may be held from the time of sampling until they are analyzed. Table II has been restructured in this final regulation to correlate with the parameters in the new Tables IA, IB, IC, ID, and IE in Section 136.3(a). Table II allows cross-reference between the container, preservative, and holding times and the individual parameters in Tables IA, to IE.

In response to comments, several changes were made in Table II of the final regulations for prescribed container materials, preservation requirements, and holding times of wastewater samples. Where supported by comments, changes were made primarily in holding times. In response to comments, EPA has adopted the requirement that some samples be

analyzed immediately, to avoid sample degradation. This would be as soon as the sample is collected and labelled, generally within 15 minutes. Longer holding times are generally not appropriate where the sample may quickly degrade. However, a longer time period may be justified under the variance procedure. Exhibits 3 and 4, below, show that for organic compounds and pesticides, the holding times were generally extended from 30 days after extraction to 40 days after extraction. Changes were also made to enable a single sample to be used for analyses of extractable organics and of pesticides. This was a step towards the goal of uniformity, sought by EPA and by the commenters.

Table II as promulgated also allows a variance to holding times under § 136.3(e). Analysts may exceed the holding times if they have data on file to show that the specific types of samples are stable for a longer time and if they receive a variance from the Regional Administrator.

No changes were made for container materials, preservation requirements, or holding times in final Table II from the proposed requirements for the biological parameters listed in Table IA, or the radiological parameters listed in Table IE. Changes which were made in Table II for inorganic parameters listed in Table IB, organic parameters listed in Table IC, and pesticide parameters listed in Table ID are summarized in the following Exhibits 2, 3, and 4, of this preamble. Proposed and final container materials, preservation requirements, and holding times in Exhibits 2, 3, and 4 are given only for the affected pollutant parameters in Tables IB, IC and ID of the regulation.

EXHIBIT 2.—CHANGES MADE IN TABLE II FOR TABLE IB PARAMETERS

Parameter	Requirement	Change	
		From (proposed)	To (final)
Chlorine residual	Holding time	2 hours	Analyze immediately.
Cyanide	Preservative	Na ₂ S ₂ O ₃	Ascorbic acid. Add: Remove sulfide as cadmium sulfide.
pH	Holding time	2 hours	Analyze immediately.
Chromium VI	Holding time	48 hours	24 hours.
Mercury	Preservative	0.05% K ₂ Cr ₂ O ₇	Delete.
Organic carbon	Preservative	None	Add: HCl or H ₂ SO ₄ to pH < 2.
Dissolved oxygen probe	Holding time	1 hour	Analyze immediately.
Winkler	Preservative		Add: Store in dark.
Phenols	Container	P and G	G only.
Residue, total	Holding time	14 days	7 days.
Residue, filterable	Holding time	14 days	7 days.
Residue, settleable	Holding time	7 days	48 hours.
Sulfide	Preservative		Add: NaOH to pH > 9.
	Holding time	28 days	7 days.
Sulfite	Holding time	48 hours	Analyze immediately.
	Preservative	Cool to 4 °C	None required.

EXHIBIT 3.—CHANGES MADE IN TABLE II FOR TABLE IC PARAMETERS

Parameter	Requirement	Change	
		From (proposed)	To (final)
Chlorinated organic compounds.....	(?)	(?)	(?)
Purgeable aromatics.....	Preservative.....		Add: HCl to pH < 2. Samples not receiving pH treatment must be analyzed within 7 days.
Acrolein and acrylonitrile.....	Holding time.....	3 days.....	14 days.
Phenols ¹	Preservative.....	H ₂ SO ₄ to	Deleted.
	Holding time.....	pH < 2 30 days after extraction.	40 days after extraction.
Benzidine ¹	Preservative.....		Add: pH 2-7, if 1,2-diphenylhydrazine is present, adjust pH to 4.0 ± 0.2.
Phthalate esters ¹	Preservative.....	Na ₂ S ₂ O ₅	Deleted.
	Holding time.....	30 days after extraction.....	40 days after extraction.
Nitrosamines ¹	Preservative.....		Add: Store in dark.
	Holding time.....	30 days after extraction.....	40 days after extraction, adjust pH 7-10 for diphenylnitrosamine.
PCBs ¹	Preservative.....	Na ₂ S ₂ O ₅	Deleted.
	Holding time.....	30 days after extraction.....	40 days after extraction.
Nitroaromatics and isophorone ¹	Preservative.....	Na ₂ S ₂ O ₅	Deleted.
	Holding time.....	30 days after extraction.....	40 days after extraction.
Polynuclear aromatic hydrocarbons ¹	Preservative.....		Add: Store in dark.
	Holding time.....	30 days after extraction.....	40 days after extraction.
Haloethers ¹	Preservative.....		40 days after extraction.
Chlorinated hydrocarbons ¹	Preservative.....	Na ₂ S ₂ O ₅	Deleted.
	Holding time.....	30 days after extraction.....	40 days after extraction.
TCDD ¹	Holding time.....	30 days after extraction.....	40 days after extraction.

¹ The following optional preservation may be used when the asterisked categories are to be analyzed in a single sample: cool to 4 °C; add 0.008% Na₂S₂O₅; store in dark; adjust pH 6.0-8.0.

² Deleted as a parameter—see Purgeable Halocarbons and Chlorinated Hydrocarbons.

EXHIBIT 4.—CHANGES MADE IN TABLE II FOR TABLE ID PARAMETERS

Parameter	Requirement	Change	
		From (proposed)	To (final)
Pesticides ¹	Preservative.....	Na ₂ S ₂ O ₅	Deleted.
	Holding time.....	30 days after extraction.....	Add: pH 5-9. 40 days after extraction.

¹ The following optional preservation may be used when the asterisked categories are to be analyzed in a single sample: cool to 4 °C; add 0.008% Na₂S₂O₅; store in dark; adjust pH 6.0-8.0.

F. Incorporation by Reference

The analytical methods approved are lengthy and detailed. Many are readily available to the public. Thus, § 136.3(a) has been revised to show that the full texts of the test procedures taken from the various references in Tables IA, IB, IC, ID and IE are "incorporated by reference" into the regulatory language of these Guidelines in accordance with the regulations of the Office of the Federal Register, and with the approval of the Director of the Office of the Federal Register. Methods which are not readily available are printed in full as appendices to this notice.

As a convenience to the users, § 136.3(b) has also been added. This cross-references Tables IA, IB, IC, ID, and IE and the parameters therein. It cites specific references, the sources from which they may be readily acquired, and indicates, where available, approximate costs of the references.

The full texts of the test procedures cited are available for inspection only at the Office of the Federal Register Information Center, Room 8301, 1100 L Street, NW., Washington, D.C. Full texts of non-copyrighted and copyrighted test procedures are available from the sources indicated in § 136.3(b).

To accommodate this new paragraph (b), paragraphs (b) and (c) in the existing regulation have been redesignated as paragraphs (c) and (d), respectively.

V. Public Participation and Response to Most Significant Comments

Two hundred and twenty letters, many with attachments of data and other information, were received in response to the Administrator's December 1979 request for comments. Ten additional letters were received in response to the reopened comment period in January 1981. Letters were received from industries, Federal and State agencies, industrial and trade associations, universities, testing laboratories, research institutes, engineering and consulting firms, local government agencies, standards and professional organizations, and from one private citizen.

To facilitate analysis, comments within the letters were classified into three categories—policy, technical, and general, and then into thirteen sub-categories. The comments were then reviewed by a technical group of EPA analytical experts and by an EPA policy review group. The record contains a response to the comments, organized on the basis of these subcategories. The

final rulemaking today incorporates changes based upon this review. This section highlights significant and generic comments and EPA responses.

In the following paragraphs of this section only issues of major concern will be discussed. Many lesser technical questions or minor issues which were raised are discussed in the "Response to Comments" document contained in the record.

A. GC, HPLC, and GC/MS Test Procedures

1. Policy on Applicability of Test Procedures

EPA requested comments on the general applicability of the proposed methods. To present the best state-of-the-art test procedures for analyzing trace organic pollutants in industrial wastewaters, EPA specifically requested commenters to share their experiences and data relative to sensitivity, precision, accuracy, and detection limits of the proposed GC, HPLC, and GC/MS test procedures.

Comment: Several commenters felt that the EPA should not publish some of these test procedures (specifically, the GC, HPLC, and the GC/MS) as regulations until they had been fully validated by multi-laboratory studies.

Response: No data or information were provided to the EPA in the comments that would permit revisions of the texts of the proposed test procedures to better represent the state-of-the-art, to enhance general applicability, or to preclude interference problems. Consequently, EPA believes these GC, HPLC, and GC/MS test procedures to be the best state-of-the-art test procedures currently available for the analysis of wastewater discharges for the priority toxic organic pollutants.

The multi-laboratory validation studies for Methods 601-602, 604-613, 624, and 625 have been completed and support the general applicability of these test procedures to the analysis of treated wastewater effluents. Since the front-end chemistry of the GC/MS test procedures, i.e., sample preservation, holding times, and purge and trap or methylene chloride extraction, are similar for the GC and the GC/MS test procedures, it would be expected that the precision and accuracy of these test procedures will be substantially the same over the concentration ranges which give linear detector responses. This has been substantiated by the validation studies.

Comment: Several commenters felt that GC, HPLC, and GC/MS test procedures did not meet rigorous criteria, such as those of the consensus standards organizations, had not been precisely written, and did not meet the state-of-the-art.

Response: The Agency recognizes that these test procedures include some state-of-the-art techniques which have not been as widely used as the consensus methods which were approved and promulgated in 1973 and 1976. But for Methods 601-602, 604-613, 624, 625, 1624, and 1625, method performance is now supported by the multi-laboratory validation studies. These 16 test procedures are now backed by data which meet criteria at least as rigorous as that employed by consensus standards organizations.

Only single-laboratory data are available for 4 parameters (2-chloroethylvinyl ether, 1,2-Dichloropropane, cis-1,3-Dichloropropene, and trans-1,3-Dichloropropene) in Method 601, 2 parameters (acrolein and acrylonitrile) in Method 603, 1 parameter (Hexachlorocyclopentadiene) in Method 612, and 5 parameters (Bromomethane, 2-chloroethylvinyl ether, 1,2-Dichloropropane, cis-1,3-Dichloropropene, and trans-1,3-dichloropropene) in Method 624. It was necessary to resort to single-laboratory testing due to the long-term instability of these parameters in the Youden pair

samples used in the multi-laboratory validation studies. In many instances these single-laboratory evaluated test procedures have been more exhaustively tested for their applicability to industrial wastewaters than the currently approved test procedures in these guidelines which are cited from consensus sources.

The procedures promulgated today, as written, most precisely define the current state-of-the-art for the analysis of trace organic compounds in wastewater discharges. No better methods are now available for general use.

Comment: Several commenters said that these test procedures had not been demonstrated by the Agency to be generally applicable to all wastewater effluents.

Response: These test procedures were developed by single laboratories to be applicable under various conditions of preservation and holding times, to samples taken from wastewaters which were shown in various surveys to have the compounds of interest. Their general applicability to multiple industrial wastewater effluents is now corroborated by the multi-laboratory validation studies, which specifically searched for matrix effects. In specific cases of interference, analysts may seek leave to use alternative procedures under 40 CFR 136.4.

Comment: Several commenters suggested that these test procedures be issued as "interim test procedures" without regulatory impact within the limits of their analytical uncertainties.

Response: This comment was made prior to the completion of the multi-laboratory validation studies. Acceptable performance for these methods is now verified for analysis of industrial wastewater effluents. Mandatory quality control within the text of the test procedures further strengthens their credible applicability to effluent analysis. When spike or surrogate recoveries are poor (do not fall within the acceptable performance levels for the parameters of concern), the method will not have produced data acceptable for NPDES reporting purposes such as permit applications and discharge monitoring reports demonstrating compliance.

Comment: Several commenters felt that the test procedures should be continually reevaluated to ensure they are kept abreast of the state-of-the-art. They requested that the test procedures be re-submitted for comment and peer review after the 20-laboratory validation tests were completed.

Response: The Agency decision to conduct the 20-laboratory validation

studies was made in the spirit expressed by these commenters. The studies have been completed, and their results are incorporated in the revised texts of these test procedures. These results corroborate the general applicability of the validated test procedures to multiple wastewater effluents. EPA may amend 40 CFR Part 136, if comments or future results of these studies suggest that this is necessary. EPA is accepting comment on the actual calculation of specific control limits.

2. Flexibility and Analysts' Professional Judgment

EPA requested commenters' experiences and opinions on the flexibility that should be incorporated within the GC, GC/MS, and HPLC procedures. Optimum flexibility would render the test procedures most generally applicable to industrial discharges, without seriously compromising data quality.

After careful study, EPA has found most of the comments received in response to this request to have merit and has reacted positively to them.

Comment: Several commenters requested that test procedures be revised to allow the analyst maximum leeway to exercise professional judgment to adapt the test procedures to the sample at hand. They felt that defining test procedures in terms of "good laboratory practices" and analytical criteria would allow the incorporation of technological advances not permitted in rigidly structured procedures. The commenters specifically requested flexibility in GC temperature programming and extraction solvent stripping procedures.

Response: Where technically justified, the proposed test procedures have been relaxed to allow flexibility for analysts to exercise professional judgment. This flexibility is being incorporated within the text of the GC and HPLC procedures, in recognition of the rapid advances occurring in the state-of-the-art for packed and open tubular columns. A primary configuration of GC or HPLC components is described within the test procedure. However, to optimize the applicability of the chromatographic technique to analytical requirements unique to specific discharges, the analyst is allowed to use professional judgment in selecting packed or open tubular columns, operating temperature programs, carrier gas or solvent flow rates, and detectors. Analysts may also use their discretion in selecting cleanup procedures. EPA has also relaxed the strict protocol for sample extract concentration. In the proposed test

procedures, sample extracts were concentrated by means of a Kuderna-Danish concentrator, which consists of a concentrator tube, an evaporative flask, and a Snyder column. Many studies comparing the Kuderna-Danish concentration technique to a variety of others have provided no statistically conclusive support for the rigid protocol for most materials tested. Accordingly, within the scope of the GC, HPLC, and GC/MS test procedures, analysts are permitted some discretion in selection of concentration techniques.

Comment: Other commenters said these analytical criteria for the test procedures should be in terms of mandatory verification and quality control procedures.

Response: The EPA agrees. With the added flexibility in test procedures for analyst discretion, an added responsibility is borne by the analyst for mandatory quality control and validation procedures. These requirements have long been recognized as elements of good analytical laboratory practices. Accordingly, Methods 601-613, 624, and 625 now incorporate verification and quality control and the criteria for reportable analytical results for regulatory purposes.

Comment: Many of the commenters were concerned with the costs associated with rigidly prescribed methods, especially where required use of several such methods would call for significant capital expenditures in highly specialized equipment.

Response: The flexibility which has been incorporated into the test procedures is expected to encourage rapid incorporation of technical advances, and to allow the dischargers to select the most cost-effective analytical options when acquiring major analytical equipment. However, any modifications of Methods 601-613, 624, 625, 1624, and 1625, which are not expressly permitted in the text of the methods as given in Appendix A to this part, will be considered major modifications and must be approved as alternate test procedures under the provisions of §§ 136.4 and 136.5.

Sample preservation and holding times have also been standardized to allow the same sample to be used for more than one method. This flexibility allows monitoring costs to be minimized and existing equipment to be fully utilized. Additionally, contract laboratory services are available when the analytical load of a discharger does not justify purchase of specialized analytical equipment (See cost discussion below).

General Response to Comments on Flexibility and Analysts' Professional Judgment: Flexibility is permitted only in discretionary elements of the chromatographic test procedures. Changes in non-discretionary elements of the test procedures are outside the scope of the flexibility provision. Change may be made only when conditions of analytical equivalency are demonstrated within the provisions of §§ 136.4 and 136.5 of this regulation. For all discretionary changes which analysts may make, their laboratory records should corroborate that the quality of the data generated meets all stated performance criteria of precision and accuracy. (See 40 CFR 122.21, 122.41, 122.44 and 403.12).

3. Quality Control and Quality Assurance

This issue is integrally related to the preceding discussion of allowable flexibility. The availability of rigorous quality control criteria is what allows the flexibility now built into the methods. Conversely, the allowance for modification based on professional judgment makes it essential that there be a procedure for assuring that those modifications do not undermine the quality of reported data.

EPA proposed, within the test procedures, that method blanks should be processed each time a set of samples was to be extracted, or whenever there was a change in reagents. This was to safeguard against chronic laboratory contamination. EPA also proposed that standard quality assurance practices be used. The practices proposed included field replicates to validate the precision of the sampling technique, laboratory replicates to validate the precision of the analysis, and special (or fortified) samples to validate the accuracy of the analysis. If doubt existed in the identification of any peak in a gas chromatogram, the proposed quality assurance required a confirmation by use of a technique such as MS. In addition, Appendix III of the proposal required an intensive quality control plan for the GC/MS test procedures. The Agency requested comments on the proposed levels of quality assurance/quality control (QA/QC) and on any additional levels that should be specified in the test procedures or left to the discretion of the analyst.

Comments: Most commenters, including several large industrial associations, restricted their comments to the operational details of the suggested programs, thus implying acceptance of the concept of the mandatory quality control procedures.

Others specifically urged adoption of such procedures.

Some commenters addressed the issue of appropriate costs and number of samples that should be analyzed for continuing QA/QC. One corporation suggested that 10%-20% of cost was reasonable, with one control sample for 10 samples analyzed. A trade association stated the QA/QC should not exceed 20% of the analytical costs. Another corporation suggested 10% spiked samples and duplicate analysis of all purgeable samples. A permitting authority suggested that 15%-20% QA/QC was reasonable.

Some commenters specified that mandatory QC should be an integral part of all of the proposed organic test procedures. There were no objections to the required analysis of four spiked reagent water samples, as proposed in Appendix III.

Response: The comments have confirmed EPA's belief that a reasonable level of mandatory quality assurance should be incorporated in all of the test procedures for organic priority pollutants to assure that data of known and acceptable quality are produced.

The analyst must demonstrate correct use of the method, reagents, and equipment before analyzing samples. Users of Methods 601-613, 624, 625, 1624, and 1625 must demonstrate their ability to generate data of acceptable quality by analyzing four spiked aliquots of reagent water containing each parameter of interest, and meeting performance specifications based upon the multiple-laboratory methods studies completed by the Agency. For a limited number of parameters discussed earlier, the performance specifications are based upon other laboratory test data. Reagent water is used to ensure that there are no matrix effects in this preliminary test.

On-going quality assurance for Methods 601-612 consists of mandatory spiking of 10% of all samples (spiking with the compounds being measured) and comparing the degree and precision of spike recovery with the test procedure criteria established in the multiple-laboratory methods studies. This will lead to a QA/QC cost in the range of 10% of the analytical costs. For Method 613, samples must be spiked with isotopically labeled 2,3,7,8-TCDD internal standards. For Methods 624 and 625 the requirement is for a 5% mandatory spiking of samples. See Section IV B above.

Users of these methods are required to spike all samples with surrogates. These QA/QC procedures are

essentially the same as those proposed except that criteria are now specified in more detail and specific control limits are based upon multiple-laboratory studies. If the recovery of any parameter falls outside the control limits, the laboratory performance for that parameter is inconsistent with control, and the analytical results for that parameter in the unspiked sample are suspect and may not be reported for regulatory compliance purposes.

If the performance criteria for the GC, HPLC, and GC/MS test procedures which have been reprinted in full text in Appendix A of this part cannot be attained in a specific wastewater matrix, the analyst may consult the Director of EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, for technical assistance. If the method must be modified beyond its allowable flexibility to meet the performance criteria, the procedures of § 136.4(b) are available.

Although these requirements for quality assurance and control are minimum EPA standards, analysts are expected to perform significantly better in almost all cases. They are also encouraged to participate in additional performance testing to assure continued analytical proficiency.

B. ICP Method

EPA proposed the ICP instrumental test procedure as an alternative to the approved test procedures for elemental analysis (such as the AA and colorimetric test procedures). In particular, comments were solicited on the general applicability of the ICP test procedure to industrial discharges.

Comment: Some commenters thought that the detection limits given in the test procedures were unrealistic. They suggested that industrial samples would need to be concentrated before such limits could be achieved.

Response: The detection limits given in Table 1 of the ICP test procedure were taken from an EPA publication (EPA-600/4-79-017, "Inductively Coupled Plasma—Atomic Emission Spectroscopy—Prominent Lines"). These detection limits are intended as guides for instrumental limits and are published for informational purposes. The method performance in terms of precision and accuracy were determined at different concentrations of analytes in distilled water in a multi-laboratory test. These are reported in Table 4 in the ICP test procedure and are the performance standards which are required by section 12 of the test procedure for instrument quality assurance.

Comment: Some commenters thought that the ICP test procedure was not

equivalent to the AA test procedure, and especially to the furnace AA test procedure.

Response: The approved furnace AA test procedure can be used to measure concentrations lower than the ICP technique can measure. Data filed with the EPA show the equivalency of the AA and ICP test procedures across the concentration ranges that are common to the two procedures. The common ranges include the concentrations which are of regulatory concern. These comparisons were made over a number of industrial discharges and a broad concentration range.

Comment: Several commenters asked for the approval of the direct current plasma (DCP) atomic emission spectrometric method as equivalent to the ICP and AA test procedures, and requested its inclusion in Table IB as an approved test procedure for elemental analysis.

Response: EPA did not have data to show the applicability of the DCP technique to wastewater analysis and accordingly did not propose it as an alternate test procedure for elemental analysis. Data showing applicability to wastewaters were not made available by the commenters, although data were presented to show the applicability of DCP to sample matrices other than wastewater. Because of this incomplete data base, EPA was unable to include DCP in the list of approved test procedures.

Recently, a DCP manufacturer has provided such data to EPA for approval through the equivalency provisions of §§ 136.4 and 136.5, and EPA is currently considering approval of the DCP test procedure for the analysis of trace elements in wastewater.

Comment: Several commenters had difficulty understanding the guidance given for background corrections and for high dissolved solids (salt buildup) interferences.

Response: When using the ICP procedure it is important to make background corrections. The analyst must determine and incorporate into the analysis the valid correction factors for spectral interferences caused by high dissolved solids concentrations. Section 2.1 of the ICP test procedure has been revised to make this clear. Additional guidance has also been given to correct for salt buildup at the tip of the nebulizer.

Comment: Some commenters thought that the suggested combinations of elements in stock solutions were ambiguous.

Response: The mixed standard solutions suggested by the EPA in the test procedure were found to be

compatible mixtures. Other combinations may be used within the scope of the test procedure, as long as precipitations and other chemical reactions do not occur. The test procedure text has been revised to make this clear.

Comment: Some commenters felt that other wavelengths of light which were also emitted in the characteristic spectrum of the element should be permitted.

Response: Other wavelengths may be used when those given in the test procedure are obscured. In using them, the analyst must demonstrate that they are free from interfering wavelengths or that interference results can be corrected.

Comment: Several commenters presented data and suggested that antimony and thallium should be included within the scope of the ICP test procedure.

Response: Antimony and thallium are priority pollutants and the EPA agrees they should be included within the scope of the ICP test procedure since the submitted data show these metals can be recovered in excess of 90% from spiked samples using the ICP test procedure.

Comment: Several commenters requested sources from which verified outside samples could be obtained.

Response: Verified outside check samples are necessary for testing the analytical system. Upon request, the Director of EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, will either supply such samples or provide information on where quality control check samples can be obtained.

Comment: Several commenters found errors in the tables of reference wavelengths.

Response: Suggested corrections of errors in the tables and various other parts of the ICP test procedure text have been made.

Comment: Several commenters questioned the estimated costs for analyses made by the ICP test procedure, relative to other approved test procedures.

Response: Cost estimates for analysis by the ICP test procedure were given only as general comparisons with the costs of the other alternate test procedures in Table IB, which are still approved for trace metal analyses. The analyst may exercise professional judgment in selection of the approved alternate test procedure from Table IB which best meets his analytical needs. If the ICP instrument system is available to the analyst, it may well be the most

cost-effective approved alternate test procedure, especially if large numbers of samples containing several of the ICP-approved metals are to be analyzed. Otherwise, the AA or one of the other approved alternate test procedures may prove to be more cost-effective. The estimates given for the ICP analyses are average contract charges experienced by the EPA for multi-element analyses of large lots of samples.

C. (CBOD₅) Method

The Agency proposed the CBOD₅ test procedure in response to requests from environmental analysis laboratories to measure the carbonaceous BOD of wastewater without the complications caused by the nitrogenous oxygen demand.

Comments: EPA requested comments and additional data on the control of nitrification in BOD measurements. Many letters were received, several accompanied by extensive test data. A majority of the letters expressed confusion over the use of the CBOD₅ versus the traditional 5-day BOD test. None of the commenters questioned the test procedure.

Response: The CBOD₅ method (Parameter No. 14, Table IB) is being added to the list of approved measurements. This method is new, and should not be confused with the traditional 5-day BOD test which is listed in Table IB as Parameter No. 9. The nitrogen inhibitor is not a procedural option, rather CBOD₅ must be designated as the pollutant or effluent limitation that is measured to report the CBOD₅ parameter.

A discharger whose permit requires reporting the traditional 5-day biochemical oxygen demand (Parameter No. 9, Table IB) may not use a nitrogen inhibitor in the procedure for reporting results. Only when a discharger's permit explicitly states that CBOD₅ is the parameter whose monitoring is required may the permittee report data using the CBOD₅ nitrogen inhibited analytical method.

D. Table II: Required Containers, Preservation, and Holding Times

EPA proposed mandatory preservation techniques, container materials, and holding times for industrial wastewater samples. It also proposed a mechanism by which a permit holder or analytical laboratory could obtain a variance from these requirements if justified by data. The permittee or analyst was also limited to shorter holding periods, if this was necessary to maintain sample stability. In the proposed guidelines, these were paragraph 136.3(d) and footnote 4 to

Table II. These provisions are now contained in paragraph 136.3(e) and footnote 3 of Table II.

Comment: Some commenters thought that Table II was too detailed and should not be included in the text of the regulation. They suggested that EPA make it available under a separate cover.

Response: The EPA disagrees. EPA continues to believe that the integrity of the sample is critical to the quality of monitoring data. It is best presented and publicized as a requirement through inclusion in the regulation.

Comment: Several commenters felt that preservation techniques, holding times, and container materials should be presented as recommendations only. They thought the diversity of wastewater samples and sampling requirements could best be judged by the professional taking the sample.

Response: EPA agrees that the judgment of the professional taking the sample is critical to the integrity of the sample. However, after the sample is taken, sample integrity is maintained and verified only by control of container materials, preservation procedures, and holding times. Only with verifiable sample integrity can analytical data be correlated to the sample source. EPA's evaluation of NPDES monitoring practices has confirmed that inadequate sample preservation and failure to observe recommended holding times are major analytical problem areas. For these reasons EPA has included Table II in the mandatory text of this regulation.

Comment: Other commenters said that there should be more standardization of the container, holding time, and preservation requirements between parameters in order to minimize the number of samples that needed to be taken.

Response: EPA agrees that this is desirable. It is, however, secondary to quality assurance. Table II requirements have now been standardized to a significant degree. This minimizes the number of preserved samples that need to be taken.

Comment: Several commenters felt that there were stable wastewater sample types that would not require adherence to the mandatory requirements of Table II.

Response: When a permit applicant knows that Table II requirements do not apply to his wastewater—and he has data to substantiate this conclusion—the variance provisions of paragraph 136.3(e) and footnote 3 of Table II allow less stringent requirements to prevail. Such variances must be obtained from the Regional Administrator under these provisions.

General Response: Many commenters provided data or information relating to specific requirements of Table II. The changes made in Table II in response to these comments were summarized earlier in Exhibits 2, 3, and 4 in section 4(e) of this preamble.

E. Cost Estimates for Methods

EPA is concerned with the costs of analyses required by the new regulations, because of their overall importance to programs under the Clean Water Act. In the December 3, 1979, *Federal Register*, the Agency solicited comments on these costs and listed EPA's typical costs for Carbonaceous BOD, ICP, GC, HPLC, and the GC/MS analyses.

Comments: Several comments from the public addressed issues such as the high cost of routine analysis, the appropriateness of the figures presented by EPA, and the variations in cost experienced, depending upon lot size, throughput, and complexity of the analyses performed. Nearly all of the comments received were directed toward organic analyses and the related requirements for capital equipment. Several comments also seemed to rely on the erroneous assumption that the proposed methods would require separate samples for each procedure.

Response: EPA noted a wide range of unit costs cited, based largely on volume. These regulations do not require that each permittee perform its own analyses. When the small volume of analytical loads makes unit costs less economical, the permittee may use commercial laboratories, where analytical work loads can be maintained at levels which optimize costs.

EXHIBIT 5.—EPA CURRENT EXPENDITURES FOR WATER AND WASTEWATER ANALYSIS FOR PRIORITY POLLUTANTS

	Cost
113 Organic Compounds by GC/MS (includes field & laboratory blanks).....	\$800.00
Each Replicate Sample for 114 Organics by GC/MS.....	1600.00
Each Priority Pollutant Spiked Sample for 114 Organics by GC/MS (with data calculations).....	660.00
13 Elemental Compounds by AA-Flame or Flameless.....	130.00
ICP—Up to 21 Selected Elements.....	30.00
Cyanide, EPA Standard Method—Cyanide Amendable to Chlorination or Free Cyanide.....	4.50
Asbestos (transmission electron microscope analysis).....	332.00
GC (Average of costs for methods 601-612).....	100.00

¹Based upon actual prices per sample offered to the Agency for 200-sample bid lots.

²Based upon actual prices offered to the Agency for 750 ICP and 6500 AA sample bid lots.

³Based upon actual prices offered per sample to the Agency for 250-sample bid lots.

⁴Based upon actual prices per sample for 5400 samples (900 volatile, 4500 semi-volatile), averaged for three contracts with the Agency.

The Agency has compiled the data presented in Exhibit 5 from actual (lowest) contract bids, obtained through a competitive bidding process. As shown in the footnotes, they were based upon lots of specific sizes and on sample throughputs of approximately 200 samples per month for GC/MS and transmission electron microscope (for asbestos), and 100 per month for elemental analyses. The table costs were constructed on the basis of survey analysis. Permittees may expect somewhat lower costs if they are only analyzing for certain specific parameters.

A commenter making a commercial quotation places the cost of a quality assured analysis of the 111 currently designated organic toxic pollutants at \$500 per sample. However, comparison of the Agency's and other commenters' cost data has generally been impossible, since the Agency has not known the factors on which the various commenters' cost estimates were based.

The Agency has estimated analytical costs in other regulations which implement various NPDES monitoring requirements of the Clean Water Act. Analytical costs were estimated in the preambles of the Consolidated Permits Regulations (45 FR 33290, May 19, 1980) and NPDES Regulations (44 FR 34408, June 14, 1979), which are consistent with the estimates given in Exhibit 5. Analytical cost estimates consistent with those given above have also been included in promulgations of effluent limitations guidelines and pretreatment standards for individual industrial categories.

While EPA agrees with many commenters that less costly procedures would be highly desirable, the proposed methods appear to be the most cost-effective currently available. These cost estimates include 4 spiked reagent water analyses and 10% spiked sample analyses. Ongoing research by this Agency and others should produce less expensive approaches that, with testing, will prove equivalent or better, especially for analyzing trace organic toxic pollutants in industrial and municipal wastewater.

To encourage development of new, improved, and less costly analytical technologies, the Agency, by establishing the Equivalency Program (see § 136.4 and 136.5), has provided a mechanism for their rapid approval and use of new procedures.

F. Publication of Full Texts of Test Procedures

Comments: Several commenters thought that it was inappropriate for the EPA to publish the full texts of test

procedures within these guidelines. They felt that the Agency had reversed its past policy to "incorporate test procedures by reference" into these regulations.

Response: When test procedures are readily available from other sources, EPA will incorporate them by reference. However, test procedures for routine analysis of trace organic pollutants, with the exception of a few pesticidal organic chemicals, were unavailable to meet the analytical requirements for controlling priority organic pollutants. EPA developed the proposed test procedures through a high-priority research effort. For the convenience of the public and to facilitate timely comment, EPA published the full texts of the draft procedures in the preamble of the proposed regulation. In order to continue the convenience, and to ensure that the final methods are as widely distributed as the proposed methods, EPA is including, as an appendix to this amendment, the full text of the approved, Agency developed, test procedures for analysis of the priority pollutants. It is possible that in the future full text of these test procedures will become available from other sources.

In general, the text of approved test procedures will not be published in the *Federal Register* when they are readily available from other sources. EPA will continue to "incorporate approved test procedures by reference" in these guidelines as it has in the past. Methods are clearly incorporated by reference in § 136.3(a) and a new § 136.3(b) has been added to clearly identify the sources of these references. This should resolve the commenter's concerns.

G. Consistency of Analytical Methods Approved Under Different Acts

Comments: Several commenters were concerned that EPA was requiring the regulated community to use two different test procedures for analyzing similar or identical compounds, one set under the Safe Drinking Water Act, and another in these Guidelines under the Clean Water Act. They concluded that the cost of compliance with these various requirements unduly burdened the "rate payer" by what appeared to be duplication.

Response: EPA makes every effort to ensure that the analytical methods prescribed under its regulations are proliferated only when necessary. Regulations issued under different Acts are applicable to the matrices defined by those Acts. Where analytical methods are prescribed in these regulations, consideration must be given to the concentration ranges that must be

measured and the interferences to be expected.

Interferences may be unique to a matrix or may be common to several matrices covered by these Acts and regulations. Whenever possible, within the information and data available to the Agency, the same methods are approved for measuring the same parameters in the different matrices. There are many instances where this is not possible. For example, for drinking water analyses both a purge and trap procedure (Method 501.1) and an alternate solvent extraction procedure (Method 501.2) are approved for the analysis of the trihalomethanes (THM). In drinking water, interferences for THM analysis are minimal. If the drinking water extraction procedure were applied to wastewater samples for the purgeable compounds, extracts which result would present much more formidable analytical problems than would have been the case if the purge and trap procedure had been used. Therefore, it is not possible to approve the drinking water THM test procedures for the analysis of THMs and related purgeable pollutants in wastewater samples. On the other hand, Method 601 can easily be used for analysis of THMs in drinking water.

VI. Regulatory Analyses

(a) Under Executive Order 12291, EPA must judge whether a regulation is "major" and therefore subject to the requirement of a "Regulatory Impact Analysis." This regulation is not major for the following reasons: (1) It only prescribes analytical methods and sample handling requirements that ensure a uniform measure of pollutants across all wastewater discharges within minimum acceptance criteria. It does not require that analyses actually be made. The purpose is to ensure that the quality of environmental monitoring data meets certain minimum standards.

(2) The impact of this regulation will be far less than \$100 million.

(a) The regulation affects unit monitoring costs for other regulatory programs, e.g., effluent guidelines regulations and the implementation regulations of the National Pollutant Discharge Elimination System (NPDES), and the pretreatment programs. However, it does not impose those costs. In fact, the monitoring costs for other programs are considered in each other rule-making. This is appropriate because total (rather than unit) monitoring costs are determined by the monitoring provisions of those other regulations.

(b) This regulation has deliberately provided approval of several analytical options for most compounds. This often

allows NPDES permittees to select the option that is best suited to their particular monitoring requirements and that will minimize their monitoring costs. In addition, the approval of the CBOD₅ analysis will facilitate modification of CWA permits to allow treatment works and their control authorities to focus on the best measure of oxygen demand, thereby achieving treatment economies that will reduce costs of treatment significantly.

(c) Further, through the equivalency provisions, these test procedure guidelines have been designed to encourage the development of innovative analytical methods by the private sector and to encourage the competitive viability of the instrument manufacturing industry. The equivalency provision also allows individual dischargers to gain approval of analytical systems of their own design that may further reduce their total monitoring costs.

(3) The impact of compliance with these regulations will not be concentrated on any particular sectors of American industry.

This regulation was submitted to the Office of Management and Budget (OMB) for review as required by Executive Order 12291. Any comments from OMB to EPA and any EPA response to those comments will be available for public inspection at the Public Information Reference Unit, Room M2904 (EPA Library—Rear), TM-213, Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460, Phone: (202) 382-5926, Office Hours 8:00 a.m. to 4:30 p.m.

(b) Under the Regulatory Flexibility Act, 5 U.S.C. 601 et seq., EPA is required to determine whether a regulation will significantly affect a substantial number of small entities so as to require a regulatory analysis. The regulation requires no new reports beyond those already now required. The analytical techniques approved here either can be handled by small facilities, or are widely available by contract at a reasonable price. Therefore, in accordance with 5 U.S.C. 605(b), I hereby certify that this rule will not have a significant adverse economic impact on a substantial number of small facilities.

(c) The equivalency information provision in this rule has been submitted for approval to the Office of Management and Budget (OMB) under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 et seq. It is not effective until OMB approves it and a technical amendment to that effect will be published in the *Federal Register*.

VII. Effective Dates

The effective date of this rule is January 22, 1985 for all methods except the method for CBOD₅. This date, 90 days hence, was chosen to allow analysts sufficient time to learn of the new methods and to implement the necessary changes in laboratory practices. After January 24, 1985, data reported to EPA must be generated using the methods approved under 40 CFR Part 136, including these methods added by today's amendment.

An effective date of 30 days, November 26, 1984, was chosen for using the method for CBOD₅. This is the only method for a new parameter. Treatment works and permitting authorities are eager to begin measurement and analysis for this new parameter because it may result in achieving treatment economies and reduce costs significantly. Although data reported to permitting authorities or EPA on this parameter must be generated using this method after 30 days, there is no requirement that any treatment works monitor for this parameter or use the new method until a treatment works applies for and receives a permit modification. Permits may be modified after EPA's amendment to the secondary treatment rule is effective. The amended secondary treatment rule should be effective before or on the same day that today's rule approving the CBOD₅ method is effective. There is no reason why EPA should postpone the effective date of this rule for more than 30 days and possibly delay use of this method and parameter for persons whose permit can be changed quickly.

The Director of the *Federal Register* has approved all materials which are "incorporated by reference" in the text of the regulation to be incorporated. They are incorporated by reference on the effective dates given above.

List of Subjects in 40 CFR Part 136

Water Pollution Control;
Incorporation by reference.

Dated: September 26, 1984.

William D. Ruckelshaus,
Administrator.

Regulation

For the reasons set out in the Preamble, Part 136, Chapter 1, Subchapter D of Title 40, Code of Federal Regulations, is amended as set forth below. Only new provisions are being promulgated at this time; unchanged provisions are reprinted for the purpose of clarity.

1. The authority citation for Part 136 is revised to read as follows:

Authority: Sections 301, 304(h), 307 and 501(a), Pub. L. 95-217, 91 Stat. 1566, et seq. (33 U.S.C. 1251, et seq.) (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

2. In paragraphs 136.1 (a) and (c), reference to the Federal Water Pollution Control Act Amendments of 1972 (FWPCA) is replaced by reference to the Clean Water Act of 1977, and applicability under paragraph 136.1(a) is extended to Parts 122-125 of Title 40. As revised, paragraphs (a) and (c) of § 136.1 read as follows:

§ 136.1 Applicability.

(a) An application submitted to the Administrator, or to a State having an approved NPDES program for a permit under § 402 of the Clean Water Act of 1977, as amended (CWA), and/or to reports required to be submitted under NPDES permits or other requests for quantitative or qualitative effluent data under Parts 122 to 125 of Title 40, and,

(c) Certifications issued by States pursuant to § 401 of the CWA, as amended.

3. In § 136.2, paragraph (a) is revised to reference the Clean Water Act of 1977, and paragraphs (f), (g), and (h) are removed, and a new paragraph (f) is added defining "Detection limit," and paragraphs (g) and (h) are reserved, as follows:

§ 136.2 Definitions.

As used in this part, the term:

(a) "Act" means the Clean Water Act of 1977, Pub. L. 95-217, 91 Stat. 1566, et seq. (33 U.S.C. 1251 et seq.) (The Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977).

(f) "Detection limit" means the minimum concentration of an analyte (substance) that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero as determined by the procedure set forth at Appendix B of this Part.

(g) [Reserved.]

(h) [Reserved.]

4. In § 136.3, Table I is restructured into five new tables by transferring the biological parameters formerly designated as parameters 4, 5, 6, 7 and 8 to new Table IA, entitled "List of Approved Biological Test Procedures," by adding an additional EPA reference to the approved test procedures, and by updating the references to Standard Methods and USGS: by transferring the inorganic parameters formerly designated as parameters 1-3, 10-13, 15-

93, 96-98, and 104-115 to new Table IB, entitled "List of Approved Inorganic Test Procedures", adding two new inorganic parameters, Carbonaceous Biochemical Oxygen Demand (CBOD₅) and Nitrate-Nitrite, including an additional test procedure based upon the inductively coupled plasma technique in Table IB for 25 of the metal parameter designations, by including 10 methods approved under the equivalency provisions of §§ 136.4(d) and 136.5(e), and updating references to EPA, Standard Methods, ASTM, AOAC and USGS test procedures; by deleting

former parameter 14 (Chlorinated organic compounds) and by entering the individual chlorinated organic compounds into new Table IC, entitled, "List of Approved Test Procedures for Non-Pesticide Organic Compounds", transferring old parameters 9 (Benzidine) and 94 (Pentachlorophenol) to Table IC, by including the 78 additional proposed non-pesticidal organic parameters and by adding 17 new test procedures in Table IC; by deleting former parameter 95 (Pesticides) and by entering the 68 individual pesticides into new Table ID,

entitled "List of Approved Test Procedures for Pesticides", by including the 2 additional proposed pesticide parameters, and the two new test procedures in Table ID; and by transferring the former radiological parameters 99-103 to new Table IE, entitled "Approved Radiological Test Procedures", adding an EPA reference to the approved test procedures, and updating the Standard Methods, ASTM and USGS references. As revised, Table I reads as follows:

§ 136.3 Identification of Test Procedures.

TABLE IA.—LIST OF APPROVED BIOLOGICAL TEST PROCEDURES

Parameter and units	Method *	EPA *	Reference (Method Number or Page)		
			Standard Methods 15th Ed.	ASTM	USGS
Bacteria:					
1. Coliform (fecal) number per 100 ml.....	MPN, 5 tube, 3 dilution; or, membrane filter (MF) *, single step.....	p. 132.....	980C.....		B-0050-77
2. Coliform (fecal) in presence of chlorine number per 100 ml.....	MPN, 5 tube, 3 dilution.....	p. 124.....	909C.....		
3. Coliform (total, number per 100 ml.....	MPN, 5 tube, 3 dilution; or, MF * single step or two step.....	p. 132.....	908C.....		
		p. 114.....	908A.....		B-0025-77.
4. Coliform (total) in presence of chlorine, number per 100 ml.....	MPN, 5 tube, dilution; or MF * with enrichment.....	p. 108.....	909A.....		
		p. 114.....	908A.....		
5. Fecal streptococci, number per 100 ml.....	MPN, 5 tube, 3 dilution; MF *; or, plate count.....	p. 111.....	909 (A + A.5c).....		B0055-77.*
		p. 139.....	910A.....		
		p. 136.....	910B.....		
		p. 143.....	910C.....		

Table IA Notes

* The method must be specified when results are reported.

* Microbiological Methods for Monitoring the Environment, Water and Wastes, 1978", EPA-600/8-78-017, U.S. Environmental Protection Agency.

* Greeson, P.E., et al., Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples, "U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A4, Laboratory Analysis, 1977.

* 0.45 µm membrane filter or other pore size certified by the manufacturer to fully retain organisms to be cultivated, and free of extractables which could interfere with their growth and development.

* Approved only if dissolution of the KF Streptococcus Agar (Section 5.1, USGS Method 8-0055-77) is made in a boiling water bath to avoid scorching of the medium.

TABLE 1B.—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter, units, and method	Reference (method No. or page)				
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	Other
1. Acidity, as CaCO ₃ , mg/L: Electrometric end point or phenolphthalein end point	305.1	402(4.d)	D1067-70(E)		
2. Alkalinity, as CaCO ₃ , mg/L: Electrometric or colorimetric:					
Titration to pH 4.5, manual	310.1	403	D1067(B)	I-1030-78	P. 548. ²
Or automated	310.2			I-2030-78	
3. Aluminum—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	202.1	303C		I-3051-78	
AA furnace	202.2	304			Method 200.7. ⁴
Inductively coupled plasma					
Or colorimetric (Eriochrome cyanine R)		306B			
4. Ammonia (as N), mg/L: Manual distillation ⁵ (at pH 9.5):					
Followed by	350.2	417A			
Nesslerization	350.2	417B	D1426-79(A)	I-3520-78	P. 553. ²
Titration	350.2	417D			
Electrode	350.3		D1426-79(D)		
Automated phenate, or	350.1	417F	D1426-79(C)	I-4523-78	
Automated electrode					
5. Antimony—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	204.1	303A			
AA furnace, or	204.2	304			Method 200.7. ⁴
Inductively coupled plasma					
6. Arsenic—Total ³ mg/L:					
Digestion ³ followed by	206.5				
Hydride	206.3	303E	D2972-78(B)	I-3062-78	
AA furnace	206.2	304			
Inductively coupled plasma					
Or colorimetric (SDDC)	206.4	307B	D2972-78(A)	I-3060-78	Method 200.7. ⁴
7. Barium—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	208.1	303C			
AA furnace, or	208.2	304		I-3084-78	
Inductively coupled plasma					Method 200.7. ⁴
8. Beryllium—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	210.1	303C	D3645-78	I-3095-78	
AA furnace	210.2	304			

TABLE 1B.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	Other
Inductively coupled plasma Or colorimetric (aluminum).....		309B			Method 200.7. ⁴
9. Biochemical oxygen demand (BOD ₅), mg/L: Winkler (Azide modification)..... Or electrode method.....	405.1	507		I-1578-78	P. 17. ⁸ P. 548. ⁹
10. Boron—Total, mg/L: Colorimetric (curcumin) or Inductively coupled plasma.....	212.3	404A		I-3112-78	Method 200.7. ⁴ P. S44. ¹⁰
11. Bromide, mg/L: Titrimetric.....	320.1		D1246-77(C)	I-1125-78	
12. Cadmium—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration..... AA furnace..... Inductively coupled plasma..... Voltammetry ⁴ or..... Colorimetric (Dithizone).....	213.2 213.2	303A or 303B 304	D3557-78 (A or B)	I-3135-78 or I-3136-78	Pg. 557. ⁸ P. 37. ⁹ Method 200.7. ⁴
13. Calcium—Total ² , mg/L: Digestion ³ followed by: Atomic absorption..... Inductively coupled plasma..... Or EDTA titration.....	215.1 215.2	303A 311C 507(5.e.6)	D511-77(C) D511-77(B)	I-3152-78	Method 200.7. ⁴
14. Carbonaceous Biochemical oxygen demand (CBOD ₅), mg/L: Winkler (Azide modification) or electrode method with nitrification inhibitor.....					
15. Chemical oxygen demand (COD), mg/L: Titrimetric colorimetric..... Manual or..... Automated..... Spectrophotometric.....	410.1 410.2 410.3 410.4	508A	D1252-78	I-3560-78 I-3562-78 I-3561-78	P. 550 ⁸ and P. 17 ⁹ and (1 ¹⁰)
16. Chloride, mg/L: Titrimetric (silver nitrate) or Mercuric nitrate..... Colorimetric (ferricyanide) manual or Automated.....	325.3 325.1 or 325.2	407A 407B 407D	D512-67(B) D512-67(A) D512-67(C)	I-1183-78 I-1184-78 I-1187-78 I-2187-78	P. 554. ⁸
17. Chlorine—Total residual, mg/L: Titrimetric-mercurimetric ¹² Starch end point..... Iodometric or..... DPD-FAS..... Spectrophotometric, DPD, or Electrode.....	330.1 330.2 330.3 330.4 330.5	408C 408B 408A 408D 408E	D1253-76(A) D1253-76(B)		(1 ¹¹)
18. Chromium VI dissolved, mg/L: 0.45 micron filtration with: Extraction and atomic absorption, or Colorimetric (Diphenylcarbazide).....	218.4	303B		I-1232-78 I-1230-78	
19. Chromium—Total ² , mg/L: Digestion ³ (optional extraction) followed by: AA direct aspiration..... AA furnace..... Inductively coupled plasma..... Or colorimetric (Diphenylcarbazide).....	218.3 218.1 218.2	303A or 303B 304	D1687-77(D)	I-3236-78	P. 557. ⁸ Method 200.7. ⁴
20. Cobalt—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration..... AA furnace, or..... Inductively coupled plasma.....	219.1 219.2	303A or 303B 304	D3558-77 (A or B)	I-3240-78 or I-3239-78	P. 37. ⁸ Method 200.7. ⁴
21. Color, platinum Cobalt units or dominant wavelength hue, luminance, purity: Colorimetric, ADMI..... Platinum cobalt, or..... Spectrophotometric.....	110.1 110.2 110.3	204D 204A 204B		I-1250-78	(1 ¹²)
22. Copper—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration..... AA furnace..... Inductively coupled plasma..... Colorimetric (Neocuproine)..... Bicinchoninate.....	220.1 220.2	303A or 303B 304	D1688-77 (D or E)	I-3271-78 or I-3270-78	P. 557 ⁸ and P. 37. ⁹ Method 200.7. ⁴
23. Cyanide—Total, mg/L: Manual distillation with MgCl ₂ Followed by titrimetric..... Manual or..... Automated ¹³ spectrophotometric.....	335.2 335.2 335.2 335.3	412D 412B 412C 412D 412F	D2036-75(A) D2036-75(A) D2036-75(B)	I-3300-78	(1 ¹³)
24. Cyanide amenable to chlorination, mg/L: Manual distillation with MgCl ₂ . Followed by titrimetric, manual or automated ¹³ spectrophotometric.	335.1				
25. Fluoride—Total, mg/L: Manual distillation ¹⁴ Followed by manual or..... Automated electrode..... SPADNS..... Or automated complexone.....	340.2 340.1 340.3	413A 413B 413C 413E	D1179-72(B) D1179-72(A)	I-4327-78	P. 22. ⁸
26. Gold—Total ² , mg/L: Digestion ³ followed by: AA direct aspiration..... Or AA furnace.....	231.1 231.2	303A 304			
27. Hardness—Total as CaCO ₃ , mg/L: Automated colorimetric..... EDTA titration..... Inductively coupled plasma..... Or atomic absorption (sum of Ca and Mg as their respective carbonates)	130.1 130.2 215.1+ 242.1	314B 303A	D1126-67(B)	I-1338-78 I-3153-78+ I-3448-78	Method 200.7. ⁴

TABLE 1B.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	Other
28. Hydrogen ion (pH), pH units: Electrometric	150.1	423	D1293-78(A) or D1293-78(B).	I-1586-78	
Measurements; or automated electrode					(1 ^a)
29. Indium—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	235.1	303A			
Or AA furnace	235.2	304			
30. Iron—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	236.1	303A or 303B	D1068-77 (C or D)	I-3381-78	P. 557. ^a
AA furnace	236.2	304			
Inductively coupled plasma					Method 200.7. ^a
Or colorimetric (Phenanthroline)		315B	D1068-77(A)		(1 ^a)
31. Kjeldahl nitrogen—Total (as N), mg/L: Digestion and distillation	351.3	420A or B			P. 552. ^a
Followed by titration	351.3	417D	D3590-77		
Nesslerization or	351.3	417B			
Electrode	351.3	417E		I-4551-78	
Automated phenate	351.1			I-4552-78	
Semi-automated block digester	351.2				
Or potentiometric	351.4				
32. Lead—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	239.1	303A or 303B	D3559-78 (A or B)	I-3399-78	P. 557. ^a
AA furnace	239.2	304			
Inductively coupled plasma					Method 200.7. ^a
Voltammetry ^a or			D3559-78(C)		
Colorimetric (Dithizone)		316B			
33. Magnesium—Total ^a , mg/L: Digestion ^a followed by: Atomic absorption	242.1	303A	D511-77(B)	I-3447-78	P. 557. ^a
Inductively coupled plasma					Method 200.7. ^a
Or gravimetric		316B	D511-77(A)		
34. Manganese—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	243.1	303A or 303B	D858-77 (B or C)	I-3454-78	P. 557. ^a
AA furnace	243.2	304			
Inductively coupled plasma					Method 200.7. ^a
Or colorimetric (Persulfate)		319B	D858-77(A)		P. 564. ^a
Periodate					18.
35. Mercury—Total ^a , mg/L: Cold vapor, manual or	245.1	303F	D3223-79	I-3462-78	P. 559. ^a
Automated	245.2				
36. Molybdenum—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	246.1	303C		I-3490-78	
AA furnace, or	246.2	304			
Inductively coupled plasma					Method 200.7. ^a
37. Nickel—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	249.1	303A or 303B	D1886-77 (C or D)	I-3499-78	
AA furnace	249.2	304			
Inductively coupled plasma					Method 200.7. ^a
Or colorimetric (Heptoxime)		321B			
38. Nitrate (as N), mg/L: Bicine sulfate, or	352.1		D092-71		P. 554. ^a
Nitrate-nitrite N minus Nitrite N	See parameters 39 and 40.	See parameters 39 and 40.	See parameters 39 and 40.	See parameters 39 and 40.	P. 28. ^a
39. Nitrate-nitrite (as N), mg/L: Cadmium reduction, manual	353.3	418C	D3867-79(B)		
Or automated; or	353.2	418F	D3867-79(A)	I-4545-78	
Automated hydrazine	353.1				
40. Nitrite (as N), mg/L: Spectrophotometric, manual or	354.1	419	D1254-67		19.
Automated (Diazotization)				I-4540-78	
41. Oil and grease—Total recoverable, mg/L: Gravitric (extraction)	413.1	503A			
42. Organic carbon—Total (TOC), mg/L: Combustion or oxidation	415.1	505	D2579-78(A) or D2579-78(B).		P. 551. ^a and P. 4. ³⁰
43. Organic nitrogen (as N), mg/L: Total Kjeldahl N minus ammonia N	See parameters 31 and 4.	420A	D3590-77 minus D1426-79(A).	See parameters 31 and 4.	PP. 552-53. ^a
44. Orthophosphate (as P), mg/L: Ascorbic acid method, automated	365.1	424G		I-4601-78	P. 561. ^a
Or manual single reagent or	365.2	424F	D515-78(A)		
Manual two reagent	365.3				
45. Osmium—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration, or	252.1	303C			
AA furnace	252.2	304			
46. Oxygen, dissolved, mg/L: Winkler (Azide modification)	360.2	421B	D1589-60(A)	I-1575-78	P. 550. ^a
Or electrode	360.1	421F		I-1576-78	
47. Palladium—Total ^a , mg/L: Digestion ^a followed by: AA direct aspiration	253.1				P. 527. ^a
Or AA furnace	253.2				P. 528. ^a
48. Phenols, mg/L: Manual distillation	420.1		D1783-70 (A or B)		28.
Followed by manual	420.1				26.
Or automated ^{1a} colorimetric (4AAP)	420.2				21.
49. Phosphorus (elemental), mg/L: Gas-liquid chromatography.					

TABLE 1B.—LIST OF APPROVED INORGANIC TEST PROCEDURES—Continued

Parameter, units, and method	Reference (method No. or page)				Other
	EPA 1979	Standard methods 15th Ed.	ASTM	USGS ¹	
50. Phosphorus—Total, mg/L:					
Persulfate digestion	365.2	424C (III)			P. 561. ²
Followed by manual or	365.2 or 365.3	424F	D515-78(A)		
Automated ascorbic acid	365.1	424G		I-4800-78	
Reduction; or semi-automated block digester	365.4			I-4803-78	
51. Platinum—Total ³ , mg/L: Digestion ³ followed by:					
AA direct aspiration	255.1	303A			
Or AA furnace	255.2	304			
52. Potassium—Total ³ , mg/L: Digestion ³ followed by:					
Atomic absorption	258.1	303A		I-3630-78	P. 560. ²
Inductively coupled plasma					Method 200.7. ⁴
Or flame photometric		322B	D1428-64(A)		
53. Residue—total, mg/L: Gravimetric, 103-105°C	160.3	209A		I-3750-78	
54. Residue—filterable, mg/L: Gravimetric, 180°C	160.1	209B		I-1750-78	
55. Residue—nonfilterable, (TSS), mg/L: Gravimetric, 103-105°C post washing of residue	160.2	209D		I-3765-78	
56. Residue—settleable, mg/L: Volumetric (Imhoff cone) or gravimetric	160.5	209F			
57. Residue—volatile, mg/L: Gravimetric, 550°C	160.4	209E		I-3753-78	
58. Rhodium—Total ³ , mg/L: Digestion ³ followed by:					
AA direct aspiration	265.1	303A			
Or AA furnace	267.2	304			
59. Ruthenium—Total ³ , mg/L: Digestion ³ followed by:					
AA direct aspiration	267.1	303A			
Or AA furnace	267.2	304			
60. Selenium—Total ³ mg/L: Digestion ³ followed by:					
AA furnace	270.2	304			Method 200.7. ⁴
Inductively coupled plasma					
Or hydride	270.3	303E	D3859-79	I-3667-78	
61. Silica—Dissolved, mg/L: 0.45 micron filtration:					
Followed by manual or					
Automated colorimetric (Molybdenosilicate), or					
Inductively coupled plasma					Method 200.7. ⁴
62. Silver—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	272.1	303A or 303B		I-3720-78	P. 557. ² and p. 37. ²
AA furnace, or	272.1	304			Method 200.7. ⁴
Inductively coupled plasma					
63. Sodium—Total ³ , mg/L: Digestion ³ followed by:					
Atomic absorption	273.1	303A		I-3735-78	P. 561. ²
Inductively coupled plasma					Method 200.7. ⁴
Or flame photometric			D1428-64(A)		
64. Specific conductance, mhos/cm: Wheatstone bridge	120.1	205	D1125-77(A)	I-1780-78	P. 547. ²
65. Sulfate (as SO ₄), mg/L:					
Automated methylthymol blue	375.2			I-2822-78	
Gravimetric, or	375.3	426A or 426B	D516-68(A)		PP. 562-63. ²
Turbidimetric	375.4	426C	D516-68(B)		
66. Sulfide (as S), mg/L:					
Titrimetric (iodine) or	376.1	427D		I-3840-78	
Colorimetric (methylene blue)	376.2	427C			
67. Sulfite (as SO ₃), mg/L: Titrimetric (iodine iodate)	377.1	428F	D1339-78(C)		
68. Surfactants, mg/L: Colorimetric (methylene blue)	425.1	512A	D2330-68(A)		
69. Temperature, °C: Thermometric	170.1	212			(**).
70. Thallium—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	279.1	303A			
AA furnace, or	279.2	304			
Inductively coupled plasma					Method 200.7. ⁴
71. Tin—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration or	282.1	303A		I-3850-78	
AA furnace	282.2	304			
72. Titanium—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration or	283.1	303C			
AA furnace	283.2	304			
73. Turbidity, NTU: Nephelometric	180.1	214A	D1889-71	I-3860-78	
74. Vanadium—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	286.1	303C			
AA furnace	286.2	304			
Inductively coupled plasma					Method 200.7. ⁴
Or colorimetric (Gallic acid)			D3373-75		
75. Zinc—Total ³ mg/L: Digestion ³ followed by:					
AA direct aspiration	289.1	303A or 303B	D1691-77(D)	I-3900-78	P. 557. ²
AA furnace	289.2	304	D1691-77(C)		P. 37. ²
Inductively coupled plasma					Method 200.7. ⁴
Or colorimetric (Zincon)					²⁴ .

Table 1B Notes

¹ "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments," U.S. Department of the Interior, U.S. Geological Survey, Open-File Report 78-679, or "Methods for Determination of Inorganic Substances in Water and Fluvial Sediments," N.W. Skougstad, *et al*, U.S. Geological Survey, Techniques of Water-Resources Investigation, Book 5, Chapter A1, 1979.

² "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 13th ed. (1980).

³ For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes, 1979." One (§ 4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (§ 4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all sample types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion and in all cases the method write-up should be consulted for specific instructions and/or cautions.

Note: If the digestion procedure for direct aspiration or graphite furnace atomic absorption analysis included in one of the other approved references is different than the above, the EPA procedure must be used.

Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the referenced procedure for total metals must be followed. Sample digestion of the filtrate for dissolved metals, or digestion of the original sample solution for total metals may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses provided the sample has a low COD and the filtrate meets the following criteria:

- (a) Is visibly transparent
- (b) Has no perceptible odor, and
- (c) Is free of particulate or suspended matter following acidification.

¹³⁶ The full text of Method 200.7, "Inductively Coupled Plasma Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes," is given at Appendix C of this Part 10591.

¹³⁷ Manual distillation is not required if comparability data on representative effluent samples are on company file to show that this preliminary distillation step is not necessary; however, manual distillation will be required to resolve any controversies.

¹³⁸ Ammonia, Automated Electrode Method, Industrial Method Number 379-75WE, dated February 19, 1976, Technicon AutoAnalyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.

¹³⁹ Carbonaceous biochemical oxygen demand (CBOD₅) must not be confused with the traditional BOD₅ test which measures "total BOD". The addition of the nitrification inhibitor is not a procedural option, but must be included to report the CBOD₅ parameter. A discharger whose permit requires reporting the traditional CBOD₅ may not use a nitrification inhibitor in the procedure for reporting the results. Only when a discharger's permit specifically states CBOD₅ is required can the permittee report data obtained using the nitrification inhibitor.

¹⁴⁰ American National Standard on Photographic Processing Effluents, Apr. 2, 1975, Available from ANSI, 1430 Broadway, New York, NY 10018.

¹⁴¹ The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.

¹⁴² Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

¹⁴³ COD Method, Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, Texas 77840.

¹⁴⁴ The back titration method will be used to resolve controversy.

¹⁴⁵ National Council of the Paper Industry for Air and Stream Improvement, Inc., Technical Bulletin 253, December 1971.

¹⁴⁶ Copper, Bicinchoninate Method, Method 8506, Hach Handbook of Water Analysis, 1979, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

¹⁴⁷ After the manual distillation is completed, the auto-analyzer manifolds in EPA Methods 335.03 (Cyanide) or 420.2 (phenols) are simplified by connecting the re-sample line directly to the sampler. When using the manifold setup shown in Method 335, the buffer 6.2 should be replaced with the buffer 7.6 found in Method 335.2.

¹⁴⁸ Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon Auto-Analyzer II, Technicon Industrial Systems, Tarrytown, New York 10591.

¹⁴⁹ Iron, 1,10-Phenanthroline Method, Method 8008, 1980, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

¹⁵⁰ Manganese, Periodate Oxidation Method, Method 8034, Hach Handbook of Wastewater Analysis, 1979, pages 2-113 and 2-117, Hach Chemical Company, Loveland, Colorado 80537.

¹⁵¹ Nitrogen, Nitrite, Method 8507, Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.

¹⁵² Goertzel, D., Brown, E., "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A3, p.4 (1972).

¹⁵³ R.F. Addison and R.G. Ackman, "Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography," Journal of Chromatography, Vol. 47, No. 3, pp. 421-426, 1970.

¹⁵⁴ Recommended methods for the analysis of silver in industrial wastewaters at concentrations of 1 mg/L and above are inadequate where silver exists as an inorganic halide. Silver halides such as the bromide and chloride are relatively insoluble in reagents such as nitric acid but are readily soluble in an aqueous buffer of sodium thiosulfate and sodium hydroxide to a pH of 12. Therefore, for levels of silver above 1 mg/L, 20 mL of sample should be diluted to 100 mL by adding 40 mL each of 2 M Na₂S₂O₃ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below 1 mg/L the recommended method is satisfactory.

¹⁵⁵ Stevens, H.H., Ficks, J.F., and Smoot, G.F., "Water Temperature-Influential Factors, Field Measurement and Data Presentation," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 1, Chapter D1, 1975.

¹⁵⁶ Zinc, Zincon Method, Method 8009, Hach Handbook of Water Analysis, 1979, pages 2-231 and 2-333, Hach Chemical Company, Loveland, Colorado 80537.

¹⁵⁷ "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).

¹⁵⁸ The approved method is that cited in *Standard Methods for the Examination of Water and Wastewater*, 14th Edition. The colorimetric reaction is conducted at a pH of 10.0 ± 0.2. The approved methods are given on pp. 576-61 of the 14th Edition: Method 510A for distillation, Method 510B for the manual colorimetric procedure, or Method 510C for the manual spectrophotometric procedure.

¹⁵⁹ ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977, Orion Research Incorporated, 840 Memorial Drive, Cambridge, Massachusetts 02138.

TABLE IC.—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS

Parameter ¹	EPA Method Number ^{2, 3}			Other
	GC	GC/MS	HPLC	
1. Acenaphthene.....	610	625, 1625	610	
2. Acenaphthylene.....	610	625, 1625	610	
3. Acrolein.....	603	624, 1624		
4. Acrylonitrile.....	603	624, 1624		
5. Anthracene.....	610	625, 1625	610	
6. Benzene.....	602	624, 1624		
7. Benzidine.....		625, 1625	605	Note 3, p. 1;
8. Benzo(a)anthracene.....	610	625, 1625	610	
9. Benzo(a)pyrene.....	610	625, 1625	610	
10. Benzo(b)fluoranthene.....	610	625, 1625	610	
11. Benzo(ghi)perylene.....	610	625, 1625	610	
12. Benzo(k)fluoranthene.....	610	625, 1625	610	
13. Benzyl Chloride.....				Note 3, p. 130; Note 6, p. S102.
14. Benzyl Butyl Phthalate.....	606	625, 1625		
15. Bis(2-chloroethoxy) methane.....	611	625, 1625		
16. Bis(2-chloroethyl) ether.....	611	625, 1625		
17. Bis(2-ethylhexyl) phthalate.....	606	625, 1625		
18. Bromodichloromethane.....	601	624, 1624		
19. Bromoform.....	601	624, 1624		
20. Bromomethane.....	601	624, 1624		
21. 4-Bromophenylphenyl ether.....	611	625, 1625		
22. Carbon tetrachloride.....	601	624, 1624		Note 3, p. 130;
23. 4-Chloro-3-methylphenol.....	604	625, 1625		
24. Chlorobenzene.....	601, 602	624, 1624		Note 3, p. 130;
25. Chloroethane.....	601	624, 1624		
26. 2-Chloroethylvinyl ether.....	601	624, 1624		
27. Chloroform.....	601	624, 1624		Note 3, p. 130;
28. Chloromethane.....	601	624, 1624		
29. 2-Chloronaphthalene.....	612	625, 1625		
30. 2-Chlorophenol.....	604	625, 1625		
31. 4-Chlorophenylphenyl ether.....	611	625, 1625		
32. Chrysene.....	610	625, 1625	610	
33. Dibenz(a,h)anthracene.....	610	625, 1625	610	
34. Dibromochloromethane.....	601	624, 1624		
35. 1,2-Dichlorobenzene.....	601, 602, 612	624, 625, 1625		
36. 1,3-Dichlorobenzene.....	601, 602, 612	625, 1624, 1625		
37. 1,4-Dichlorobenzene.....	601, 602, 612	625, 1625	605	
38. 3,3'-Dichlorobenzidine.....				
39. Dichlorodifluoromethane.....	601			
40. 1,1-Dichloroethane.....	601	624, 1624		
41. 1,2-Dichloroethane.....	601	624, 1624		
42. 1,1-Dichloroethene.....	601	624, 1624		
43. trans-1,2-Dichloroethene.....	601	624, 1624		
44. 2,4-Dichlorophenol.....	604	625, 1625		
45. 1,2-Dichloropropane.....	601	624, 1624		
46. cis-1,3-Dichloropropene.....	601	624, 1624		
47. trans-1,3-Dichloropropene.....	601	624, 1624		
48. Diethyl phthalate.....	606	625, 1625		

TABLE IC.—LIST OF APPROVED TEST PROCEDURES FOR NON-PESTICIDE ORGANIC COMPOUNDS—Continued

Parameter ¹	EPA Method Number ^{2, 3}			Other
	GC	GC/MS	HPLC	
49. 2,4-Dimethylphenol	604	625, 1625		
50. Dimethyl phthalate	606	625, 1625		
51. Di-n-butyl phthalate	606	625, 1625		
52. Di-n-octyl phthalate	606	625, 1625		
53. 2,4-Dinitrophenol	604	625, 1625		
54. 2,4-Dinitrotoluene	609	625, 1625		
55. 2,6-Dinitrotoluene	609	625, 1625		
56. Epichlorohydrin				Note 3, p. 130; Note 6, p. S102.
57. Ethylbenzene	602	624, 1624		
58. Fluoranthene	610	625, 1625	610	
59. Fluorene	610	625, 1625	610	
60. Hexachlorobenzene	612	625, 1625		
61. Hexachlorobutadiene	612	625, 1625		
62. Hexachlorocyclopentadiene	612	625, 1625		
63. Hexachloroethane	612	625, 1625		
64. Ideno(1,2,3-cd)pyrene	610	625, 1625	610	
65. Isophorone	609	625, 1625		
66. Methylene Chloride	601	624, 1624		Note 3, p. 130;
67. 2-Methyl-4,6-Dinitrophenol	604	625, 1625		
68. Naphthalene	610	625, 1625		
69. Nitrobenzene	609	625, 1625		
70. 2-Nitrophenol	604	625, 1625		
71. 4-Nitrophenol	604	625, 1625		
72. N-Nitrosodimethylamine	607	625, 1625		
73. N-Nitrosodi-n-propylamine	607	625, 1625		
74. N-Nitrosodiphenylamine	607	625, 1625		
75. 2,2-oxybis(1-chloropropane)	611	625, 1625		
76. PCB-1016	608	625		Note 3, p. 43;
77. PCB-1221	608	625		Note 3, p. 43;
78. PCB-1232	608	625		Note 3, p. 43;
79. PCB-1242	608	625		Note 3, p. 43;
80. PCB-1248	608	625		Note 3, p. 43;
81. PCB-1254	608	625		Note 3, p. 43;
82. PCB-1260	608	625		Note 3, p. 43;
83. Pentachlorophenol	604	625, 1625		Note 3, p. 140;
84. Phenanthrene	610	625, 1625	610	
85. Phenol	604	625, 1625		
86. Pyrene	610	625, 1625	610	
87. 2,3,7,8-Tetrachlorodibenzo-p-dioxin		613		
88. 1,1,2,2-Tetrachloroethane	601	624, 1624		Note 3, p. 130;
89. Tetrachloroethene	601	624, 1624		Note 3, p. 130;
90. Toluene	602	624, 1624		
91. 1,2,4-Trichlorobenzene	612	625, 1625		Note 3, p. 130;
92. 1,1,1-Trichloroethane	601	624, 1624		
93. 1,1,2-Trichloroethane	601	624, 1624		Note 3, p. 130;
94. Trichloroethene	601	624, 1624		
95. Trichlorofluoromethane	601	624		
96. 2,4,6-Trichlorophenol	604	625, 1625		
97. Vinyl Chloride	601	624, 1624		

Table IC Notes

- ¹All parameters are expressed in micrograms per liter (µg/L).
- ²The full text of Methods 601-613, 624, 625, 1624, and 1625, are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," of this Part 136.
- ³Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978.
- ⁴Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present, the preferred method for these two compounds is Method 603 or Method 1624.
- ⁵Method 625 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625, are preferred methods for these compounds.
- ⁶625, Screening only.
- ⁷Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).
- ⁸Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 601-613, 624, 625, 1624, and 1625 (See Appendix A of this Part 136) in accordance with procedures each in section 8.2 of each of these Methods. Additionally, each laboratory, on an on-going basis must spike and analyze 10% (5% for Methods 624 and 625 and 100% for methods 1624, and 1625) of all samples to monitor and evaluate laboratory data quality in accordance with sections 8.3 and 8.4 of these Methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported to demonstrate regulatory compliance.

Note.—These warning limits are promulgated as an "interim final action with a request for comments."

TABLE ID.—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹

Parameter µg/L)	Method	EPA ^{2, 3}	Standard Methods 15th Ed	ASTM	Other
1. Aldrin	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
	GC/MS	625			
2. Atrazine	GC				Note 3, p. 83; Note 6, p. S68.
3. Aminocarb	TLC				Note 3, p. 94; Note 6, p. S16.
4. Atrazine	GC				Note 3, p. 83; Note 6, p. S68.
5. Atrazine	GC				Note 3, p. 83; Note 6, p. S68.
6. Azinphos methyl	GC				Note 3, p. 25; Note 6, p. S51.
7. Barban	TLC				Note 3, p. 104; Note 6, p. S54.
8. α-BHC	GC	608	509A	D3086	Note 3, p. 7.
	GC/MS	625			
9. β-BHC	GC	608		D3086	
	GC/MS	625			
10. δ-BHC	GC	608		D3086	

TABLE ID.—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES¹—Continued

Parameter µg/L	Method	EPA ^{2,7}	Standard Methods 15th Ed	ASTM	Other
11. γ-BHC (Lindane)	GC/MS	* 625			
	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
12. Captan	GC/MS	825			
13. Carbaryl	GC		509A		Note 3, p. 7.
14. Carbofenthiol	TLC				Note 3, p. 94; Note 6, p. S60.
15. Chlordane	GC				Note 4, p. 30; Note 6, p. S73.
	GC	608	509A	D3086	Note 3, p. 7.
16. Chlorpropham	GC-MS	625			
17. 2,4-D	TLC				Note 3, p. 104; Note 6, p. S64.
18. 4,4'-DDD	GC		509B		Note 3, p. 115; Note 4, p. 35.
	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
19. 4,4'-DDE	GC-MS	625			
	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
20. 4,4'-DDT	GC/MS	625			
	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
21. Demeton-O	GC/MS	625			
22. Demeton-S	GC				Note 3, p. 25; Note 6, p. S51.
23. Diazinon	GC				Note 3, p. 25; Note 6, p. S51.
	GC				Note 3, p. 25; Note 4, p. 30; Note 6, p. S51.
24. Dicamba	GC				Note 3, p. 115.
25. Dichlofenthion	GC				Note 4, p. 30; Note 6, p. S73.
26. Dichloran	GC		509A		Note 3, p. 7.
27. Dicofof	GC			D3086	
28. Dieldrin	GC	608	509A		Note 3, p. 7; Note 4, p. 30.
	GC	625			
29. Dioxathion	GC/MS				Note 4, p. 30; Note 6, p. S73.
30. Disulfoton	GC				Note 3, p. 7; Note 6, p. S51.
31. Diuron	TLC				Note 3, p. 104; Note 6, p. S64.
32. Endosulfan I	GC	608	509A	D3086	Note 3, p. 7.
	GC/MS	* 625			
33. Endosulfan II	GC	608	509A	D3086	Note 3, p. 7.
	GC/MS	* 625			
34. Endosulfan sulfate	GC	608			
	GC	625			
35. Endrin	GC/MS	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
	GC	608			
36. Endrin aldehyde	GC/MS	* 625			
	GC	608			
	GC/MS	625			
37. Ethion	GC				Note 4, p. 30; Note 6, p. S73.
38. Fenuron	TLC				Note 3, p. 104; Note 6, p. S64.
39. Fenuron-TCA	TLC				Note 3, p. 104; Note 6, p. S64.
40. Heptachlor	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
	GC/MS	625			
41. Heptachlor epoxide	GC	608	509A	D3086	Note 3, p. 7; Note 4, p. 30; Note 6, p. S73.
42. Isodrin	GC/MS	625			
	GC				Note 4, p. 30; Note 6, p. S73.
43. Linuron	TLC				Note 3, p. 104; Note 6, p. S64.
44. Malathion	GC		509A		Note 3, p. 25; Note 4, p. 30; Note 6, p. S51.
45. Methiocarb	TLC				Note 3, p. 94; Note 6, p. S60.
46. Methoxychlor	GC		509A	D3086	Note 3, p. 7; Note 4, p. 30.
47. Mexacarbate	TLC				Note 3, p. 94; Note 6, p. S60.
48. Mirex	GC		509A		Note 3, p. 7.
49. Monuron	TLC				Note 3, p. 104; Note 6, p. S64.
50. Monuron-TCA	TLC				Note 3, p. 104; Note 6, p. S64.
51. Neburon	TLC				Note 3, p. 104; Note 6, p. S64.
52. Parathion methyl	GC		509A		Note 3, p. 25; Note 4, p. 30.
53. Parathion ethyl	GC		509A		Note 3, p. 25.
54. PCNB	GC		509A		Note 3, p. 7.
55. Perthane	GC			D3086	
56. Prometon	GC				Note 3, p. 83; Note 6, p. S68.
57. Prometryn	GC				Note 3, p. 83; Note 6, p. S68.
58. Propazine	GC				Note 3, p. 83; Note 6, p. S68.
59. Propham	TLC				Note 3, p. 104; Note 6, p. S64.
60. Propoxur	TLC				Note 3, p. 94; Note 6, p. S60.
61. Sebumeton	TLC				Note 3, p. 83; Note 6, p. S68.
62. Siduron	TLC				Note 3, p. 104; Note 6, p. S64.
63. Simazine	GC				Note 3, p. 83; Note 6, p. S68.
64. Strobane	GC				Note 3, p. 83; Note 6, p. S68.
65. Sweep	GC		509A		Note 3, p. 7.
66. 2,4,5-T	TLC				Note 3, p. 104; Note 6, p. S64.
67. 2,4,5-TP (Silvex)	GC		509B		Note 3, p. 115; Note 4, p. 35.
68. Terbutylazine	GC		509B		Note 3, p. 115.
69. Toxaphene	GC				Note 3, p. 83; Note 6, p. S68.
	GC/MS	608	509A	D3086	Note 3, p. 7; Note 4, p. 30.
70. Trifluralin	GC	625	509A		

Table ID Notes

- ¹ Pesticides are listed in this table by common name for the convenience of the reader. Additional pesticides may be found under Table IC, where entries are listed by chemical name.
- ² The full text of methods 608 and 625 are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," of this Part 136.
- ³ Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978. This EPA publication includes thin-layer chromatography (TLC) methods.
- ⁴ Methods for Analysis of Organic Substances in Water," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A3 (1972).
- ⁵ The method may be extended to include α-BHC, δ-BHC, endosulfan I, endosulfan II, and endrin. However, when they are known to exist, Method 608 is the preferred method.
- ⁶ Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).
- ⁷ Each analyst must make an initial, one-time, demonstration of their ability to generate acceptable precision and accuracy with Methods 608 and 625 (See Appendix A of this Part 136) in accordance with procedures given in Section 8.2 of each of these methods. Additionally, each laboratory, on an on-going basis, must spike and analyze 10% of all samples analyzed with

Method 608 or 5% of all samples analyzed with Method 625 to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported to demonstrate regulatory compliance.

Note.—These warning limits are promulgated as an "interim final action with a request for comments."

TABLE IE.—LIST OF APPROVED RADIOLOGICAL TEST PROCEDURES

Parameter and units	Methods	EPA ¹	Reference (method No. or page)		
			Standard Methods 15th Ed.	ASTM	USGS ²
1. Alpha-Total, pCi per liter	Proportional or scintillation counter	900.0	703	D1943-86	pp. 75 and 78. ³
2. Alpha-Counting error, pCi per liter	Proportional or scintillation counter	Appendix B	703	D1943-86	p. 79.
3. Alpha-Counting error, pCi per liter	Proportional counter	900.0	703	D1890-86	pp. 75 and 78. ³
4. Beta-Counting error, pCi per liter	Proportional counter	Appendix B	703	D1890-86	p. 79.
5. (a) Radium-Total, pCi per liter	Proportional counter	903.0	705	D2460-70	
(b) ²²⁶ Ra, pCi per liter	Scintillation counter	903.1	706	D3454-79	p. 81.

Table IE Notes

¹ "Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032 (1980 update), U.S. Environmental Protection Agency, August 1980.

² Fishman, M.J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters," U.S. Geological Survey, Open-File Report 76-177 (1976).

³ The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only the suspended portion. Therefore, the two results must be added to obtain the "total."

5. In § 136.3, paragraph (a) is revised to show that the full text of approved test procedures have been incorporated by reference, into the regulation to read as follows:

§ 136.3 Identification of test procedures.

(a) Parameters or pollutants, for which methods are approved, are listed together with test procedure descriptions and references in Tables IA, IB, IC, ID, and IE. The full text of the referenced test procedures are incorporated by reference into Tables IA, IB, IC, ID, and IE. The references and the sources from which they are available are given in paragraph (b) of this section. These test procedures are incorporated as they exist on the day of approval and a notice of any change in these test procedures will be published

in the Federal Register. The discharge parameter values for which reports are required must be determined by one of the standard analytical test procedures incorporated by reference and described in Tables IA, IB, IC, ID, and IE, or by any alternate test procedure which has been approved by the Administrator under the provisions of paragraph (d) of this section and sections 136.4 and 136.5 of this Part 136. Under certain circumstances (§§ 136.3 (b) or (c) or 40 CFR Part 401.13) other test procedures may be used that may be more advantageous when such other test procedures have been previously approved by the Regional Administrator of the Region in which the discharge will occur, and providing the Director of the State in which such discharge will occur

does not object to the use of such alternate test procedure.

6. In § 136.3, paragraphs (b) and (c) are redesignated as (c) and (d) and a new paragraph (b) is added to itemize the references which are "incorporated by reference" and to identify the sources from which they may be obtained. As added, the new paragraph (b) reads as follows:

§ 136.3 Identification of test procedures.

(b) The full texts of the methods from the following references which are cited in Tables IA, IB, IC, ID, and IE are incorporated by reference into this regulation and may be obtained from the sources identified. All costs cited are subject to change and must be verified from the indicated sources.

REFERENCES, SOURCES, AND COSTS

Table	Parameters	Reference, source and cost
IA—EPA	1-5	"Microbiological Methods for Monitoring the Environment, Water and Wastes," United States Environmental Protection Agency, EPA-600/8-78-017, 1978. Available from: ORD Publications, CERL, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
IA—Standard Methods	1-5	Standard Methods for the Examination of Water and Wastewater, Joint Editorial Board, American Public Health Association, American Water Works Association, and Water Pollution Control Federation 15th Edition, 1981. Available from: American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20036. Cost: \$50.00 including the Supplement to the Fifteenth Edition.
IB—Standard Methods	1-10, 12-46, 50-75	
ID—Standard Methods	1, 8, 11, 12, 15, 17-20, 26, 28, 32, 33, 35, 40, 41, 44, 46, 48, 52-54, 64, 66, 67, 69, 70	Ibid, 14th Edition.
IE—Standard Methods	1-5	
IB—Standard Methods	48	"Selected Analytical Methods approved and Cited by the United States Environmental Protection Agency," Supplement to the 15th Edition of Standard Methods for the Examination of Water and Wastewater (1981). Available from: American Public Health Association, 1015 Fifteenth Street, N.W., Washington, D.C. 20036. Cost: Included with the 15th Edition of Standard Methods for the examination of Water and Wastewater.
IB—Other (Standard Methods Supplement)	11, 47	
IC—Other (Standard Methods Supplement)	13, 56	"Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples," edited by P.E. Greeson, T.A. Ehlike, G.A. Irwin, B.W. Lium, and K.V. Slack: U.S. Geological Survey, Techniques of Water-Resources Investigation (USGS TWRI), Book 5, Chapter A4 (1977). Revised edition, 332 pages. Available from: U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. (Authorized agent of the Superintendent of Documents, Government Printing Office.) Cost: \$9.25. Prices are subject to change.
ID—Other (Standard Methods Supplement)	2-7, 13, 14, 16, 21-23, 25, 29-31, 37, 38, 39, 41-45, 47, 49, 50, 51, 56-63, 65, 68	
IA—U.S. Geological Survey (USGS)	1, 3, 5	"Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020 United States Environmental Protection Agency, March, 1979. Available from: ORD Publications, CERL, U.S. Environmental Protection Agency Cincinnati, Ohio 45268.
IB—EPA	1-13, 15-48, 50-75	
IB—ASTM	1, 2, 4, 6, 8, 11-13, 15-17, 19, 20, 22-25, 27, 28, 30-35, 37-40, 42-44, 46, 48, 50, 52, 60, 61, 63-65, 67, 68, 73-75	"Annual Book of Standards, Part 31, Water", American Society for Testing and Materials, 1980. Available from: American Society for Testing and Materials, 1915 Race Street, Philadelphia, PA 19103. Cost available from publisher.
ID—ASTM	1, 8-11, 15, 18-20, 27, 32, 33, 35, 40, 41, 46, 55, 69	
IE—ASTM	1-5	

REFERENCES, SOURCES, AND COSTS—Continued

Table	Parameters	Reference, source and cost
IB-USGS	2, 3, 4, 6-13, 15, 16, 18-23, 25, 27, 28, 30-40, 43, 44, 46, 50, 52-55, 57, 60-66, 71, 73, 75.	"Methods for determination of inorganic substances in water and fluvial sediments," N.W. Skougstad and others, editors: USGS-TWRI Book 5, Chapter A1, 1979. \$10.00. Available from: U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. (Authorized agent of the Superintendent of Documents, Government Printing Office). Prices are subject to change.
IB-Other (AOAC)	2, 4, 9, 12, 15, 16, 19, 22, 30-35, 38, 42-44, 46, 50, 52, 62-65, 75.	Official Methods of Analysis of the Association of Official Analytical Chemists, methods manual, 13th Edition (1980). Price: \$78.00. Available from: The Association of Official Analytical Chemists, 1111 N. 19th St., Suite 210, Arlington, VA 22209.
IB-Other (ANSI)	9, 12, 15, 20, 22, 23, 38, 62, 75	"American National Standard on Photographic Processing Effluents," April 2, 1975. Available from: American National Standards Institute, 1430 Broadway, New York, New York 10018.
IB-Other (EPA)	3, 5-8, 10, 12, 13, 19, 20, 22, 27, 30, 32-34, 36, 37, 52, 60-63, 70, 74, 75.	The full text of the inductively coupled plasma optical emission spectroscopic test procedure, Method 200.7, is printed in Appendix C of this Part 136.
IB-Other	21	"An Investigation of Improved Procedures for Measurement of Mill Effluent and Receiving Water Color," NCASI Technical Bulletin No. 253, December, 1971. Available from: National Council of the Paper Industry for Air and Stream Improvements, Inc., 260 Madison Avenue. Cost available from publisher.
IB-Other	4	Ammonia, Automated Electrode Method, Industrial Method Number 379-75WE, dated February 19, 1976, Technicon AutoAnalyzer II. Method and price available from Technicon Industrial Systems, Tarrytown, New York 10591.
IB-Other	15	Chemical Oxygen Demand, Method 8000, Hach Handbook of Water Analysis, 1979. Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	15	Oil Chemical Oxygen Demand Method. Method and price available from Oceanography International Corporation, 512 West Loop, P.O. Box 2980, College Station, Texas 77840.
IB-Other	17	ORION Research Instruction Manual, Residual Chlorine Electrode Model 97-70, 1977. Method and price available from Orion Research Incorporated, 840 Memorial Drive, Cambridge, Massachusetts 02138.
IB-Other	22	Bicinchoninate Method for Copper, Method 8506, Hach Handbook of Water Analysis, 1979. Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	28	Hydrogen Ion (pH) Automated Electrode Method, Industrial Method Number 378-75WA, October 1976, Technicon AutoAnalyzer II. Method and Price available from Technicon Industrial Systems, Tarrytown, New York 10591.
IB-Other	30	1, 10-Phenanthroline Method for Iron, Hach Method 8008. Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	34	Periodate Oxidation Method for Manganese, Method 8034, Hach Handbook for Water Analysis, 1979. Method and Price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	40	Nitrite Nitrogen, Hach Method 8507. Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	75	Zincon Method for Zinc, Method 8009, Hach Handbook for Water Analysis, 1979. Method and price available from Hach Chemical Company, P.O. Box 389, Loveland, Colorado 80537.
IB-Other	49	"Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography", by R.F. Addison and R.G. Ackman, Journal of Chromatography, Volume 47, No. 3, pp. 421-426, 1970. Available in most public libraries. Back volumes of the Journal of Chromatography are available from Elsevier/North-Holland, Inc., Journal Information Centre, 52 Vanderbilt Avenue, New York, NY 10164. Cost available from publisher.
IB-Other (USGS)	69	"Water temperature-influential factors, field measurement, and data presentation," by H.H. Stevens, Jr., J. Ficke, and G.F. Smoot: USGS-TWRI Book 1, Chapter D1. 1975. 65 pages, \$1.60. Available from: U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Prices are subject to change.
IB-Other (USGS)	42	"Methods for analysis of organic substances in water," by D. F. Goerlitz and Eugene Brown: USGS-TWRI Book 5, Chapter A3, 1972. 40 pages, \$9.00. Available from: U.S. Geological Survey, Branch of Distribution, 1200 South Eads Street, Arlington, VA 22202. Prices are subject to change.
IC-EPA	1-12, 14-55, 57-97	The full texts of Methods 601-613, 624, 625, 1624, and 1625 are printed in appendix A of this Part 136. The full text for determining the method detection limit when using the test procedures is given in Appendix B of this Part 136.
ID-Other (EPA)	1, 8-11, 15, 18, 19, 20, 28, 32-36, 40, 41, 69	"Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," Environmental Monitoring and Support Laboratory, United States Environmental Protection Agency, Cincinnati, Ohio 1978. Available from: ORD Publications, CERL, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
IE-EPA	1-5	"Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA-600/4-80-032 (1980 Update), United States Environmental Protection Agency, 1980. Available from: ORD Publications, CERL, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.
IE-USGS	1-5	"Selected Methods of the U.S. Geological Survey of Analysis of Wastewaters," by M.J. Fishman and Eugene Brown; U.S. Geological Survey Open File Report 76-77 (1976). \$13.50. Available from: U.S. Geological Survey, Branch Distribution, 1200 South Eads Street, Arlington, VA 22202.

The full texts of all the test procedures cited are available for inspection at the Office of the Federal Register Information Center, Room 8301, 1110 L Street, N.W., Washington, D.C. 20408.

7. In section 136.3 a new paragraph (e) is added together with a new Table II entitled, "Table II, Required Containers, Preservation Techniques, and Holding Times," to read as follows:

§ 136.3 Identification of test procedures.

(e) Sample preservation procedures, container materials, and maximum allowable holding times for parameters cited in Tables IA, IB, IC, ID, and IE are

prescribed in Table II. Any person may apply for a variance from the prescribed preservation techniques, container materials, and maximum holding times applicable to samples taken from a specific discharge. Applications for variances may be made by letters to the Regional Administrator in the Region in which the discharge will occur. Sufficient data should be provided to

assure such variance does not adversely affect the integrity of the sample. Such data will be forwarded by the Regional Administrator to the Director of the Environmental Monitoring and Support Laboratory in Cincinnati, Ohio for technical review and recommendations for action on the variance application. Upon receipt of the recommendations from the Director of the Environmental

Monitoring and Support Laboratory, the Regional Administrator may grant a variance applicable to the specific discharge to the applicant. A decision to approve or deny a variance will be made within 90 days of receipt of the application by the Regional Administrator.

* * * * *

TABLE II.—REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

Parameter No./name	Container ¹	Preservation ^{2,3}	Maximum holding time ⁴
Table IA—Bacterial Tests:			
1-4. Coliform, fecal and total	P, G	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁵	6 hours.
5. Fecal streptococci	P, G	do	Do.
Table IB—Inorganic Tests:			
1. Acidity	P, G	Cool, 4°C	14 days.
2. Alkalinity	P, G	do	Do.
4. Ammonia	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
9. Biochemical oxygen demand	P, G	Cool, 4°C	48 hours.
11. Bromide	P, G	None required	28 days.
14. Biochemical oxygen demand, carbonaceous	P, G	Cool, 4°C	48 hours.
15. Chemical oxygen demand	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
16. Chloride	P, G	None required	Do.
17. Chlorine, total residual	P, G	do	Analyze immediately.
21. Color	P, G	Cool, 4°C	48 hours.
23-24. Cyanide, total and amenable to chlorination	P, G	Cool, 4°C, NaOH to pH>12, 0.6g ascorbic acid ⁵	14 days. ⁶
25. Fluoride	P	None required	28 days.
27. Hardness	P, G	HNO ₃ to pH<2, H ₂ SO ₄ to pH<2	6 months.
28. Hydrogen ion (pH)	P, G	None required	Analyze immediately.
31, 43. Kjeldahl and organic nitrogen	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
Metals: ⁷			
18. Chromium VI	P, G	Cool, 4°C	24 hours.
35. Mercury	P, G	HNO ₃ to pH<2	28 days.
3, 5-8, 10, 12, 13, 19, 20, 22, 26, 29, 30, 32-34, 36, 37, 45, 47, 51, 52, 58-60, 62, 63, 70-72, 74, 75. Metals, except chromium VI and mercury.	P, G	do	6 months.
38. Nitrate	P, G	Cool, 4°C	48 hours.
39. Nitrate-nitrite	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
40. Nitrite	P, G	Cool, 4°C	48 hours.
41. Oil and grease	G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
42. Organic carbon	P, G	Cool, 4°C, HCl or H ₂ SO ₄ to pH<2	Do.
44. Orthophosphate	P, G	Filter immediately, Cool, 4°C	48 hours.
48. Oxygen, Dissolved Probe	G Bottle and top	None required	Analyze immediately.
47. Winkler	do	Fix on site and store in dark	6 hours.
48. Phenols	G only	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
49. Phosphorus (elemental)	G	Cool, 4°C	48 hours.
50. Phosphorus, total	P, G	Cool, 4°C, H ₂ SO ₄ to pH<2	28 days.
53. Residue, total	P, G	Cool, 4°C	7 days.
54. Residue, Filterable	P, G	do	48 hours.
55. Residue, Nonfilterable (TSS)	P, G	do	7 days.
56. Residue, Settlingable	P, G	do	48 hours.
57. Residue, volatile	P, G	do	7 days.
61. Silica	P	do	28 days.
64. Specific conductance	P, G	do	Do.
65. Sulfate	P, G	do	Do.
66. Sulfide	P, G	Cool, 4°C add zinc acetate plus sodium hydroxide to pH>9.	7 days.
67. Sulfite	P, G	None required	Analyze immediately.
68. Surfactants	P, G	Cool, 4°C	48 hours.
69. Temperature	P, G	None required	Analyze.
73. Turbidity	P, G	Cool, 4°C	48 hours.
Table IC—Organic Tests: ⁸			
13, 18-20, 22, 24-28, 34-37, 39-43, 45-47, 56, 66, 88, 89, 92-95, 97. Purgeable Halocarbons.	G, Teflon-lined septum	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹	14 days.
6, 57, 90. Purgeable aromatic hydrocarbons	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹ , HCl to pH2 ⁹	Do.
3, 4, Acrolein and acrylonitrile	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹ ; Adjust pH to 4-5 ¹⁰	Do.
23, 30, 44, 49, 53, 67, 70, 71, 83, 85, 98. Phenols ¹¹	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹	7 days until extraction, 40 days after extraction.
7, 38. Benzidines ¹¹	do	do	7 days until extraction ¹²
14, 17, 48, 50-52. Phthalate esters ¹¹	do	Cool, 4°C	7 days until extraction, 40 days after extraction.
72-74. Nitrosamines ^{13, 14}	do	Cool, 4°C, store in dark, 0.008% Na ₂ S ₂ O ₃ ⁹	Do.
76-82. PCBs ¹¹ acrylonitrile	do	Cool, 4°C	Do.
54, 55, 65, 69. Nitroaromatics and isophorone ¹¹	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹ store in dark	Do.
1, 2, 5, 8-12, 32, 33, 58, 59, 64, 68, 84, 86. Polynuclear aromatic hydrocarbons ¹¹	do	do	Do.
15, 16, 21, 31, 75. Haloethers ¹¹	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹	Do.
29, 35-37, 60-63, 91. Chlorinated hydrocarbons ¹¹	do	Cool, 4°C	Do.
67. TCDD ¹¹	do	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ⁹	Do.
Table ID—Pesticides Tests:			
1-70. Pesticides ¹¹	do	Cool, 4°C, pH 5-9 ¹⁵	Do.
Table IE—Radiological Tests:			
1-5. Alpha, beta and radium	P, G	HNO ₃ to pH<2	6 months.

Table II Notes

¹ Polyethylene (P) or Glass (G).

² Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

³ When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.95 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.82 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).

⁴ Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of samples under study are stable for the longer time, and has obtained a variance from the Regional Administrator under § 136.3(e). Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show that this is necessary to maintain sample stability. See § 136.3(e) for details.

⁵ Should only be used in the presence of residual chlorine.

⁶ Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

⁷ Samples should be filtered immediately on-site before adding preservative for dissolved metals.

⁸ Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

⁹ Sample receiving no pH adjustment must be analyzed within seven days of sampling.

¹⁰ The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling. When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

¹¹ If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangement to benzidine.

¹² Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxygen-free) atmosphere.

¹³ For the analysis of diphenylhydrazine, add 0.008% Na₂S₂O₄ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

¹⁴ The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% Na₂S₂O₄.

8. Appendices A, B, and C are added to Part 136 to read as follows:

APPENDIX A TO PART 136—METHODS FOR ORGANIC CHEMICAL ANALYSIS OF MUNICIPAL AND INDUSTRIAL WASTEWATER.

Method 601—Purgeable Halocarbons

1. Scope and Application

1.1 This method covers the determination of 29 purgeable halocarbons.

The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Bromodichloromethane	32101	75-27-4
Bromochloromethane	32104	75-25-2
Bromomethane	34413	74-83-9
Carbon tetrachloride	32102	56-23-5
Chlorobenzene	34301	108-90-7
Chloroethane	34311	75-00-3
2-Chloroethylvinyl ether	34576	100-75-8
Chloroform	32106	67-66-3
Chloromethane	34418	74-87-3
Dibromochloromethane	32105	124-48-1
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Dichlorodifluoromethane	34668	75-71-8
1,1-Dichloroethane	34496	75-34-3
1,2-Dichloroethane	34531	107-06-2
1,1,1-Trichloroethane	34501	75-35-4
trans-1,2-Dichloroethene	34546	156-60-5
1,2-Dichloropropane	34541	78-87-5
cis-1,3-Dichloropropene	34704	10061-01-5
trans-1,3-Dichloropropene	34699	10061-02-6
Methylene chloride	34423	75-09-2
1,1,2,2-Tetrachloroethane	34516	79-34-5
Tetrachloroethene	34475	127-18-4
1,1,1-Tetrachloroethane	34506	71-55-6
1,1,2-Tetrachloroethane	34511	79-00-5
Tetrachloroethene	39180	79-01-6
Trichlorofluoromethane	34489	75-69-4
Vinyl chloride	39715	75-01-4

1.2 This is a purge and trap gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the

primary column. Method 824 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for most of the parameters listed above.

1.3 The method detection limit (MDL, defined in Section 12.1) ¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The halocarbons are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the halocarbons are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the halocarbons onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the halocarbons which are then detected with a halide-specific detector. ^{2,3}

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic

tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105°C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ^{4,5} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: a purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.3), 7.7 cm of 2,6-diphenylene oxide polymer (Section 6.3.2), 7.7 cm of silica gel (Section 6.3.4), 7.7 cm of coconut charcoal (Section 6.3.1). If it is not necessary to analyze for dichlorodifluoromethane, the charcoal can be eliminated, and the polymer section lengthened to 15 cm. The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber must be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 200 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.3.1 Column 1—8 ft long x 0.1 in. ID stainless steel or glass, packed with 1% SP-1000 on Carbowax B (60/80 mesh) or

equivalent. This column was used to develop the method performance statements in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.3.2 Column 2—6 ft long x 0.1 in. ID stainless steel or glass, packed with chemically bonded n-octane on Porasil-C (100/120 mesh) or equivalent.

5.3.3 Detector—Electrolytic conductivity or microcoulometric detector. These types of detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1). The electrolytic conductivity detector was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.4 Syringes—5-mL glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25- μ L, 0.006 in. ID needle.

5.6 Syringe valve—2-way, with Luer ends (three each).

5.7 Syringe—5-mL, gas-tight with shut-off valve.

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrosorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap Materials:

6.3.1 Coconut charcoal—6/10 mesh sieved to 26 mesh, Barnebey Cheney, CA-580-26 lot # M-2849 or equivalent.

6.3.2 2,6-Diphenylene oxide polymer—Tenax, (60/80 mesh), chromatographic grade or equivalent.

6.3.3 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.3.4 Silica gel—35/60 mesh, Davison, grade-15 or equivalent.

6.4 Methanol—Pesticide quality or equivalent.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used

when the analyst handles high concentrations of such materials.

6.5.1 Place about 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material:

6.5.2.1 Liquid—Using a 100 μ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.5.2.2 Gases—To prepare standards for any of the six halocarbons that boil below 30 °C (bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methanol).

6.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μ g/ μ L from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20 °C and protect from light.

6.5.5 Prepare fresh standards weekly for the six gases and 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

6.6 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sections 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow

rate conditions equivalent to those given in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μ L of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25- μ L syringe with a 0.006 in. ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards can be stored up to 24 h, if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after 1 h.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.4 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes in Section 8.7 have been used successfully as internal standards, because of their generally unique retention times.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.5 and 6.6. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μ g/mL of each internal standard compound. The addition of 10 μ L of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μ g/L.

7.4.3 Analyze each calibration standard according to Section 10, adding 10 μ L of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.5 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of a QC check sample.

7.5.1 Prepare the QC check sample as described in Section 8.2.2.

7.5.2 Analyze the QC check sample according to Section 10.

7.5.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 2. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, proceed according to Section 7.5.4.

Note: The large number of parameters in Table 2 present a substantial probability that one or more will not meet the calibration acceptance criteria when all parameters are analyzed.

7.5.4 Repeat the test only for those parameters that failed to meet the calibration acceptance criteria. If the response for a parameter does not fall within the range in this second test, a new calibration curve, calibration factor, or RF must be prepared for that parameter according to Section 7.3 or 7.4.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an internal mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1) to improve the separations or lower the cost of measurements. Each time such a

modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 10 μ g/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 20 μ g/L of each parameter by adding 200 μ L of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in μ g/L, and the standard deviation of the recovery (s) in μ g/L, for each parameter of interest using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, then the system performance is unacceptable for that parameter.

Note: The large number of parameters in Table 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance

criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.3.

8.2.6.2 Beginning with Section 8.2.3, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.3.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for X; (3) calculate the range for recovery at the spike concentration as $(100 X' / T) \pm 2.44(100 S' / T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check

standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 2 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.7 The analyst should monitor both the performance of the analytical system and the

effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate halocarbons. A combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 8.5, add a volume to give 750 µg of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. Prepare a fresh surrogate spiking solution on a weekly basis. If the internal standard calibration procedure is being used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 7.4.2).

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl₂) to the empty sample bottle just prior to shipping to the sampling site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.* Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.³

10. Procedure

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and MDL that can be achieved under these conditions. An example of the separations achieved by Column 1 is shown in Figure 5. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.4 Allow the sample to come to ambient temperature prior to introducing it to the syringe. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual

air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 µL of the surrogate spiking solution (Section 8.7) and 10.0 µL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore, then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 11.0±0.1 min at ambient temperature.

10.7 After the 11-min purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4 min. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30 °C (subambient temperature, if poor peak geometry or random retention time problems persist) instead of the initial program temperature of 45 °C.

10.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.10 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.11 If the response for a peak exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and Equation 2

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

11.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water.⁹ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method is recommended for use in the concentration range from the MDL to 1000×MDL. Direct aqueous injection techniques should be used to measure concentration levels above 1000×MDL.

12.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0 to 500 µg/L.⁹ Single

operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

- 40 CFR Part 136, Appendix B.
- Bellar, T.A., and Lichtenberg, J.J. "Determining Volatile Organics at Microgram-per-Litre Levels by Gas Chromatography," *Journal of the American Water Works Association*, 66, 739 (1974).
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- "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
- "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
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- Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)
- "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
- "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)," Report for EPA Contract 68-03-2856 (in preparation).
- "Method Validation Data for EPA Method 601," Memorandum from B. Potter, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, November 10, 1983.

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
Chloromethane	1.50	5.28	0.08
Bromomethane	2.17	7.05	1.18
Dichlorodifluoromethane	2.62	nd	1.81
Vinyl chloride	2.67	5.28	0.18
Chloroethane	3.33	8.68	0.52
Methylene chloride	5.25	10.1	0.25
Trichlorofluoromethane	7.18	nd	nd
1,1-Dichloroethane	7.93	7.72	0.13
1,1-Dichloroethane	9.30	12.6	0.07
trans-1,2-Dichloroethane	10.1	9.38	0.10

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS—Continued

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
Chloroform	10.7	12.1	0.05
1,2-Dichloroethane	11.4	15.4	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
Carbon tetrachloride	13.0	14.4	0.12
Bromodichloromethane	13.7	14.6	0.10
1,2-Dichloropropane	14.9	16.8	0.04
cis-1,3-Dichloropropene	15.2	16.6	0.34
Trichloroethene	15.8	13.1	0.12
Dibromochloromethane	16.5	16.6	0.09
1,1,2-Trichloroethane	16.5	18.1	0.02
trans-1,3-Dichloropropene	16.5	18.0	0.20
2-Chloroethylvinyl ether	18.0	nd	0.13
Bromoform	19.2	19.2	0.20
1,1,2,2-Tetrachloroethane	21.6	nd	0.03
Tetrachloroethene	21.7	15.0	0.03
Chlorobenzene	24.2	18.8	0.25
1,3-Dichlorobenzene	34.0	22.4	0.32
1,2-Dichlorobenzene	34.9	23.5	0.15
1,4-Dichlorobenzene	35.4	22.3	0.24

Column 1 conditions: Carbowax B (80/80 mesh) coated with 1% SP-1000 packed in an 8 ft x 0.1 in. ID stainless steel or glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 45 °C for 3 min then programmed at 8 °C/min to 220 °C and held for 15 min.

Column 2 conditions: Porasil-C (100/120 mesh) coated with n-octane packed in a 6 ft x 0.1 in. ID stainless steel or glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 50 °C for 3 min then programmed at 6 °C/min to 170 °C and held for 4 min.

nd = not determined.

TABLE 2.—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 601*

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range P, P _s (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethylvinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.8	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
Methylene chloride	15.5-24.5	4.0	7.0-27.6	25-162
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.6	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

Q = Concentration measured in QC check sample, in µg/L (Section 7.5.3).

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

* Criteria were calculated assuming a QC check sample concentration of 20 µg/L.

Note: These criteria are based directly upon the method performance data in Table

3. Where necessary, the limits for recovery have been broadened to assure applicability

of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 601

Parameter	Accuracy, as recovery, $\bar{X}$ (µg/L)	Single analyst precision, s_x (µg/L)	Overall precision, S (µg/L)
Bromodichloromethane	1.12C-1.02	0.11 $\bar{X}$ +0.04	0.20 $\bar{X}$ +1.00
Bromoform	0.96C-2.05	0.12 $\bar{X}$ +0.58	0.21 $\bar{X}$ +2.41
Bromomethane	0.76C-1.27	0.28 $\bar{X}$ +0.27	0.36 $\bar{X}$ +0.94
Carbon tetrachloride	0.98C-1.04	0.15 $\bar{X}$ +0.38	0.20 $\bar{X}$ +0.39
Chlorobenzene	1.00C-1.23	0.15 $\bar{X}$ -0.02	0.18 $\bar{X}$ +1.21
Chloroethane	0.99C-1.53	0.14 $\bar{X}$ -0.13	0.17 $\bar{X}$ +0.63
2-Chloroethylvinyl ether*	1.00C	0.20 $\bar{X}$	0.35 $\bar{X}$
Chloroform	0.93C-0.39	0.13 $\bar{X}$ +0.15	0.19 $\bar{X}$ -0.02
Chloromethane	0.77C+0.18	0.28 $\bar{X}$ -0.31	0.52 $\bar{X}$ +1.31
Dibromochloromethane	0.94C+2.72	0.11 $\bar{X}$ +1.10	0.24 $\bar{X}$ +1.68
1,2-Dichlorobenzene	0.93C+1.70	0.20 $\bar{X}$ +0.97	0.13 $\bar{X}$ +6.13

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 601—Continued

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single analyst precision, s_x ($\mu\text{g/L}$)	Overall precision, S ($\mu\text{g/L}$)
1,3-Dichlorobenzene	$0.95C + 0.43$	$0.14\bar{X} + 2.33$	$0.26\bar{X} + 2.34$
1,4-Dichlorobenzene	$0.93C - 0.09$	$0.15\bar{X} + 0.29$	$0.20\bar{X} + 0.41$
1,1-Dichloroethane	$0.95C - 1.08$	$0.08\bar{X} + 0.17$	$0.14\bar{X} + 0.94$
1,2-Dichloroethane	$1.04C - 1.06$	$0.11\bar{X} + 0.70$	$0.15\bar{X} + 0.94$
1,1-Dichloroethene	$0.98C - 0.87$	$0.21\bar{X} - 0.23$	$0.29\bar{X} - 0.40$
trans-1,2-Dichloroethene	$0.97C - 0.16$	$0.11\bar{X} + 1.46$	$0.17\bar{X} + 1.46$
1,2-Dichloropropane *	1.00C	0.13 $\bar{X}$	0.23 $\bar{X}$
cis-1,3-Dichloropropene *	1.00C	0.18 $\bar{X}$	0.32 $\bar{X}$
trans-1,3-Dichloropropene *	1.00C	0.18 $\bar{X}$	0.32 $\bar{X}$
Methylene chloride	$0.91C - 0.93$	$0.11\bar{X} + 0.33$	$0.21\bar{X} + 1.43$
1,1,2,2-Tetrachloroethane	$0.95C + 0.19$	$0.14\bar{X} + 2.41$	$0.23\bar{X} + 2.79$
Tetrachloroethene	$0.94C + 0.06$	$0.14\bar{X} + 0.38$	$0.18\bar{X} + 2.21$
1,1,1-Trichloroethane	$0.90C - 0.16$	$0.15\bar{X} + 0.04$	$0.20\bar{X} + 0.37$
1,1,2-Trichloroethane	$0.86C + 0.30$	$0.13\bar{X} - 0.14$	$0.19\bar{X} + 0.87$
Trichloroethene	$0.87C + 0.48$	$0.13\bar{X} - 0.03$	$0.23\bar{X} + 0.30$
Trichlorofluoromethane	$0.89C - 0.07$	$0.15\bar{X} + 0.67$	$0.26\bar{X} + 0.91$
Vinyl chloride	$0.97C - 0.36$	$0.13\bar{X} + 0.65$	$0.27\bar{X} + 0.40$

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_x = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

* Estimates based upon the performance in a single laboratory.¹⁰

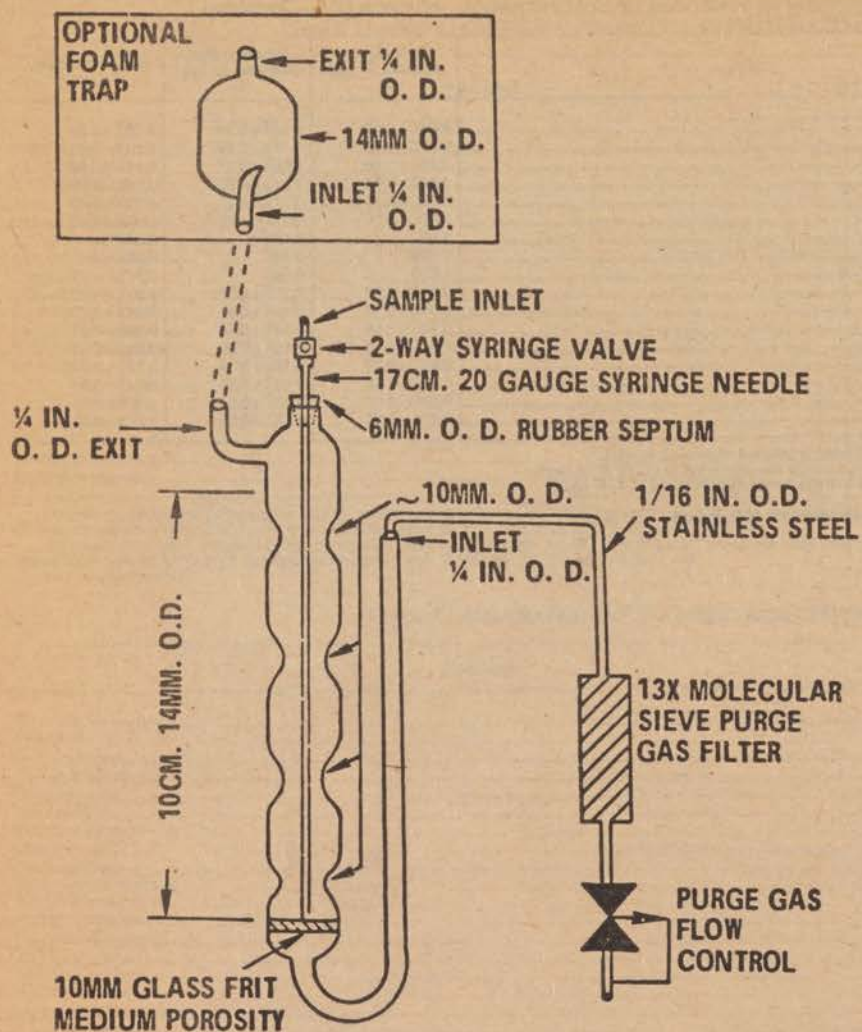


Figure 1. Purging device.

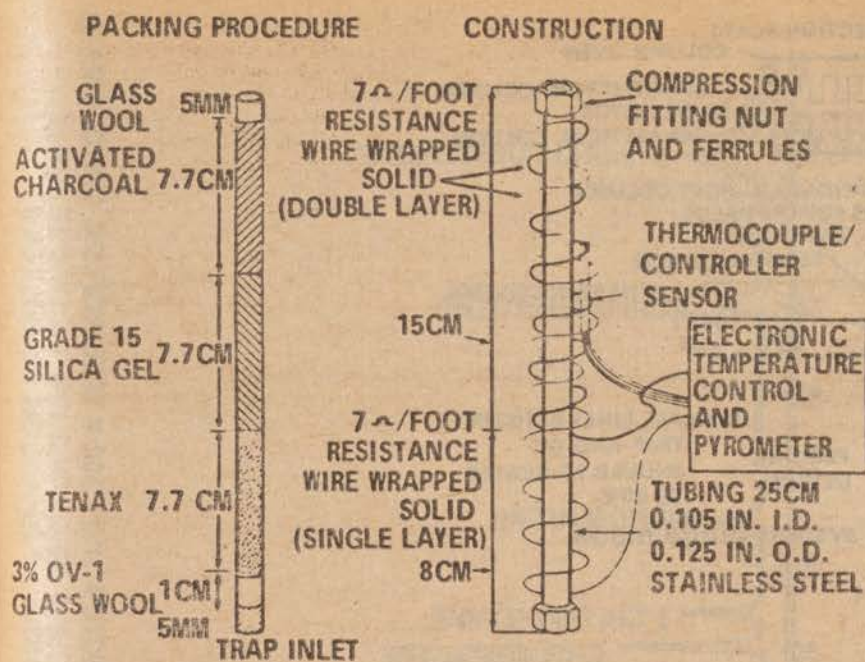


Figure 2. Trap packings and construction to include desorb capability

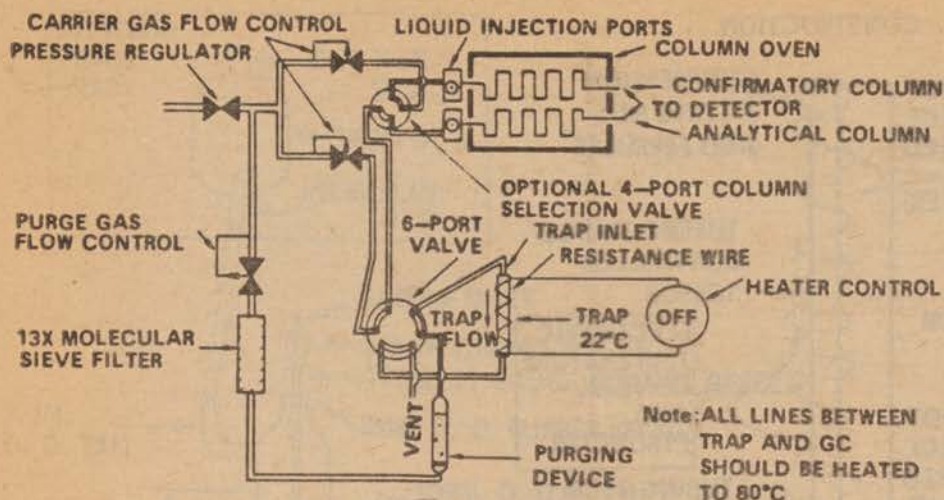


Figure 3. Purge and trap system-purge mode.

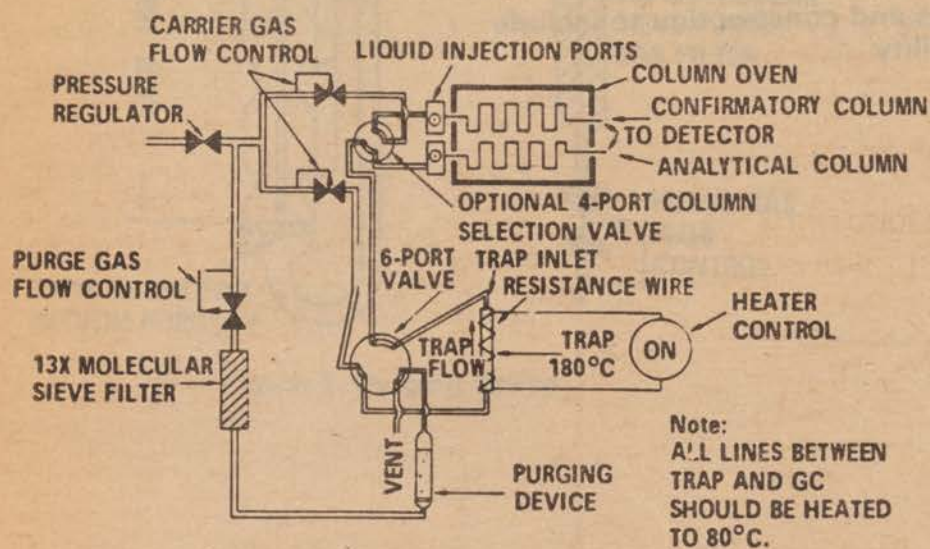


Figure 4. Purge and trap system - desorb mode.

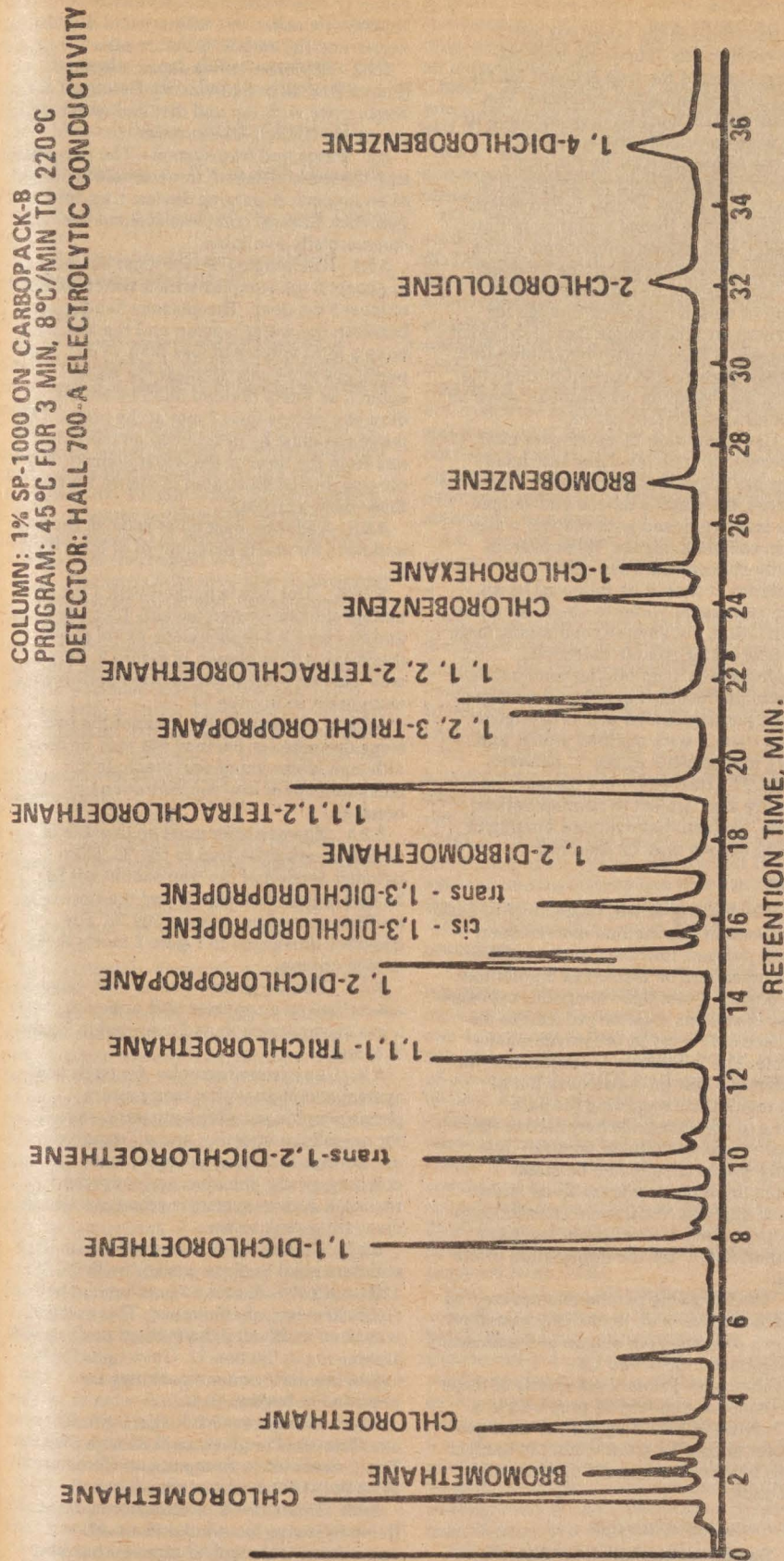


Figure 5. Gas chromatogram of purgeable halocarbons.

Method 602—Purgeable Aromatics

1. Scope and Application

1.1 This method covers the determination of various purgeable aromatics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Chlorobenzene	34301	108-90-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Ethylbenzene	34371	100-41-4
Toluene	34010	108-88-3

1.2 This is a purge and trap gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above.

1.3 The method detection limit (MDL, defined in Section 12.1) ¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the aromatics are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the aromatics onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the aromatics which are then detected with a photoionization detector. ²

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high aromatic levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105 °C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ³ for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene and 1,4-dichlorobenzene. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the

center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: A purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in.

5.2.2.1 The trap is packed with 1 cm of methyl silicone coated packing (Section 6.4.2) and 23 cm of 2,6-diphenylene oxide polymer (Section 6.4.1) as shown in Figure 2. This trap was used to develop the method performance statements in Section 12.

5.2.2.2 Alternatively, either of the two traps described in Method 601 may be used, although water vapor will preclude the measurement of low concentrations of benzene.

5.2.3 The desorber must be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 200 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3, 4, and 5.

5.3 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.3.1 Column 1—6 ft long x 0.092 in. ID stainless steel or glass, packed with 5% SP-1200 and 1.75% Bentone-34 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.3.2 Column 2—8 ft long x 0.1 in ID stainless steel or glass, packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on Chromosorb W-AW (60/80 mesh) or equivalent.

5.3.3 Detector—Photoionization detector (h-Nu Systems, Inc. Model PI-51-02 or equivalent). This type of detector has been proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop

the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.4 Syringes—5-mL glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25- μ L, 0.006 in. ID needle.

5.6 Syringe valve—2-way, with Luer ends (three each).

5.7 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.8 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrosorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Hydrochloric acid (1+1)—Add 50 mL of concentrated HCl (ACS) to 50 mL of reagent water.

6.4 Trap Materials:

6.4.1 2,6-Diphenylene oxide polymer—Tenax, (60/80 mesh), chromatographic grade or equivalent.

6.4.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.5 Methanol—Pesticide quality or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.6.1 Place about 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.6.2 Using a 100- μ L syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μ g/ μ L from the net gain in weight. When compound purity is assayed to be 90% or greater, the weight can be used without correction to calculate the concentration of the stock

standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4 °C and protect from light.

6.6.5 All standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sections 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary solution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μ L of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25- μ L syringe with a 0.006 in. ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.4 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the

compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compound, α,α,α -trifluorotoluene, recommended as a surrogate spiking compound in Section 8.7 has been used successfully as an internal standard.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Section 6.6 and 6.7. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μ g/mL of each internal standard compound. The addition of 10 μ L of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μ g/L.

7.4.3 Analyze each calibration standard according to Section 10, adding 10 μ L of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.5 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of a QC check sample.

7.5.1 Prepare the QC check sample as described in Section 8.2.2.

7.5.2 Analyze the QC check sample according to Section 10.

7.5.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 2. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, a new calibration curve, calibration factor, or RF must be prepared for that parameter according to Section 7.3 or 7.4.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of

laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentration is required containing each parameter of interest at a concentration of 10 µg/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 20 µg/L of each parameter by adding 200 µL of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter of interest using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.3.

8.2.6.2 Beginning with Section 8.2.3, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.3.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in

measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.7 The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with surrogate compounds (e.g., α , α , α -trifluorotoluene) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 6.6, add a volume to give 750 μ g of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix and dilute to volume for a concentration of 15 mg/ μ L. Add 10 μ L of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. Prepare a fresh surrogate spiking solution on a weekly basis. If the internal standard calibration procedure is being used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 7.4.2).

9. Sample Collection, Preservation, and Handling

9.1 The samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. EPA Method 330.4 or 330.5 may be used for measurement of residual chlorine.⁸ Field test kits are available for this purpose.

9.2 Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1 + 1 HCl while stirring. Fill the sample bottle in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 All samples must be analyzed within 14 days of collection.⁹

10. Procedure

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and MDL that can be achieved under these conditions. An example of the separations achieved by Column 1 is shown in Figure 6. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.4 Allow the sample to come to ambient temperature prior to introducing it to the syringe. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 μ L of the surrogate spiking solution (Section 8.7) and 10.0 μ L of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore, then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 12.0 $\pm$ 0.1 min at ambient temperature.

10.7 After the 12-min purge time, disconnect the purging device from the trap. Dry the trap by maintaining a flow of 40 mL/min of dry purge gas through it for 6 min (Figure 4). If the purging device has no provision for bypassing the purger for this step, a dry purger should be inserted into the device to minimize moisture in the gas. Attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 5), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4 min. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30 °C (subambient temperature, if poor peak geometry and random retention time problems persist) instead of the initial program temperature of 50 °C.

10.8 While the trap is being desorbed into the gas chromatograph column, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180 °C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.10 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of

actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

10.11 If the response for a peak exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(\text{RF})}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

11.2 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.⁹ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method has been demonstrated to be applicable for the concentration range from the MDL to 1000 X MDL.⁹ Direct aqueous injection techniques should be used to measure concentration levels above 1000 X MDL.

12.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1 to 550 $\mu\text{g/L}$.⁹ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample

matrix. Linear equations to describe these relationships are presented in Table 3.

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8. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine, Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Office of Research and Development, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

9. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)," Report for EPA Contract 68-03-2856 (In preparation).

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
Benzene	3.33	2.75	0.2
Toluene	5.75	4.25	0.2
Ethylbenzene	8.25	6.25	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4

Column 1 conditions: Supelcoport (100/120 mesh) coated with 5% SP-1200/1.75% Bentone-34 packed in a 6 ft x 0.085 in. ID stainless steel column with helium carrier gas at 36 mL/min flow rate. Column temperature held at 50 °C for 2 min then programmed at 8 °C/min to 90 °C for a final hold.

Column 2 conditions: Chromosorb W-AW (60/80 mesh) coated with 5% 1,2,3-Tris(2-cyanoethoxy)propane packed in a 6 ft x 0.085 in. ID stainless steel column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 40 °C for 2 min then programmed at 2 °C/min to 100 °C for a final hold.

TABLE 2.—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 602*

Parameter	Range for Q (µg/L)	Limit for s (µg/L)	Range for $\bar{x}$ (µg/L)	Range for P, P _s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in µg/L (Section 7.5.3).

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

$\bar{x}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

* Criteria were calculated assuming a QC check sample concentration of 20 µg/L.

Note: These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 602

Parameter	Accuracy, as recovery, $\bar{x}$ (µg/L)	Single analyst precision, s (µg/L)	Overall precision, S (µg/L)
Benzene	0.92C + 0.57	0.09 $\bar{x}$ + 0.59	0.21 $\bar{x}$ + 0.56
Chlorobenzene	0.95C + 0.02	0.09 $\bar{x}$ + 0.23	0.17 $\bar{x}$ + 0.10
1,2-Dichlorobenzene	0.93C + 0.52	0.17 $\bar{x}$ - 0.04	0.22 $\bar{x}$ + 0.53
1,3-Dichlorobenzene	0.96C - 0.04	0.15 $\bar{x}$ - 0.10	0.19 $\bar{x}$ + 0.09
1,4-Dichlorobenzene	0.93C + 0.09	0.15 $\bar{x}$ + 0.28	0.20 $\bar{x}$ + 0.41
Ethylbenzene	0.94C + 0.31	0.17 $\bar{x}$ + 0.46	0.26 $\bar{x}$ + 0.23
Toluene	0.94C + 0.65	0.09 $\bar{x}$ + 0.48	0.18 $\bar{x}$ + 0.71

$\bar{x}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$, in µg/L.

C = True value for the Concentration, in µg/L.

$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

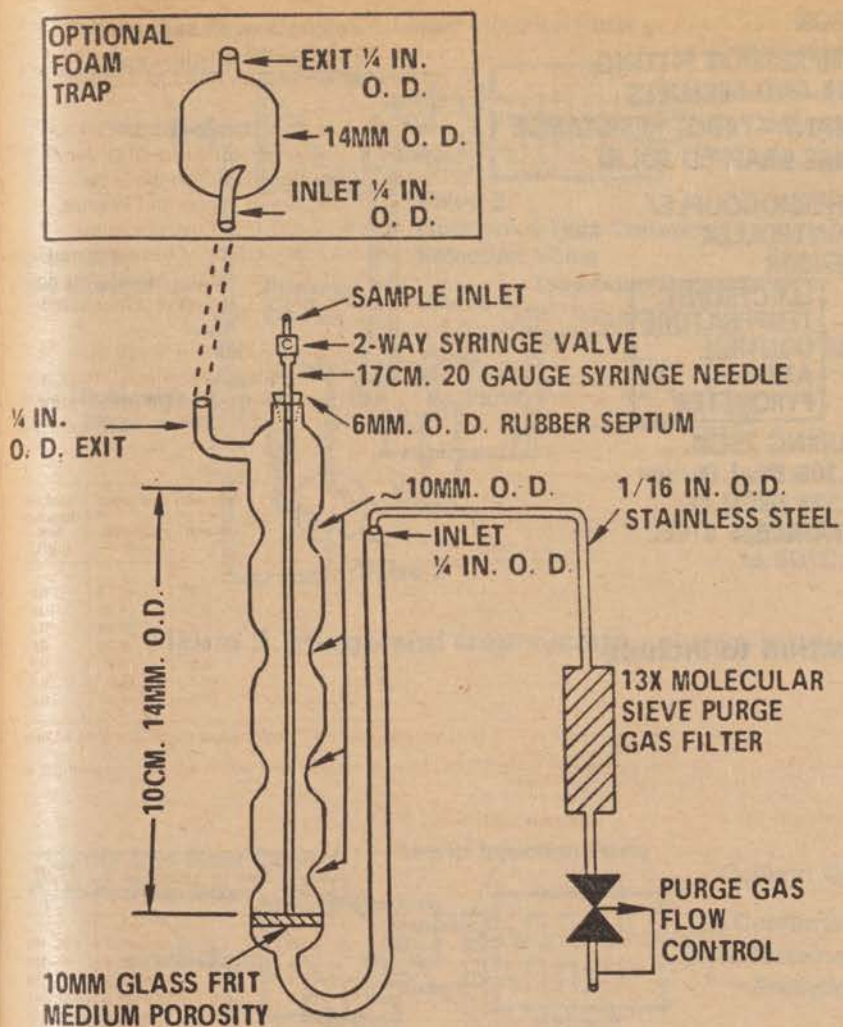


Figure 1. Purging device.

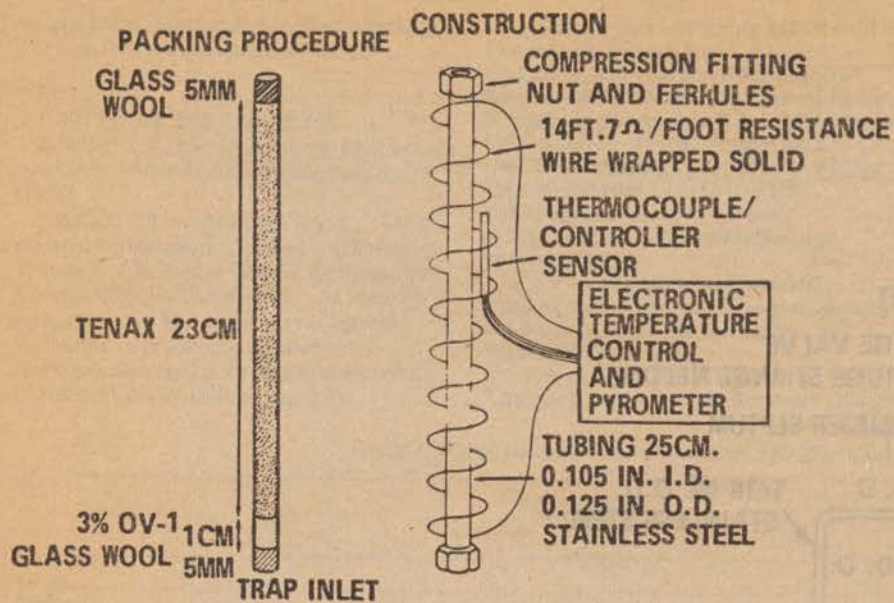


Figure 2. Trap packings and construction to include desorb capability.

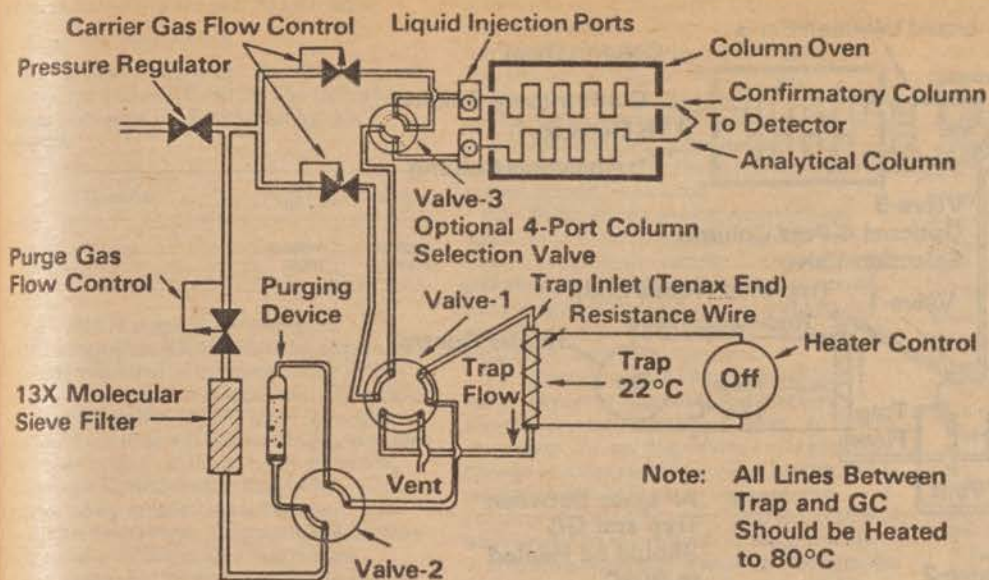


Figure 3. Purge and trap system - purge mode.

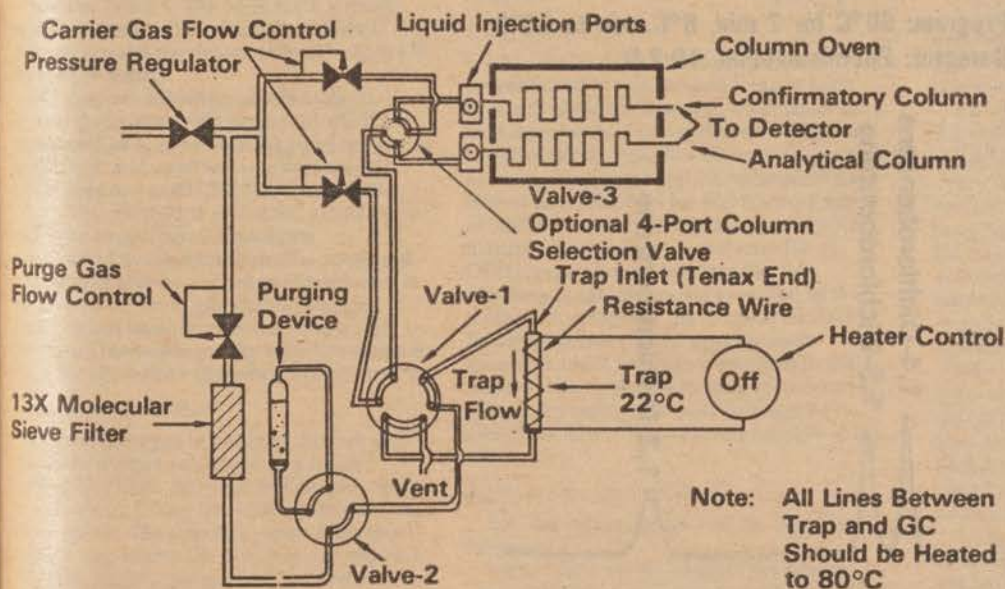


Figure 4. Purge and trap system-dry mode.

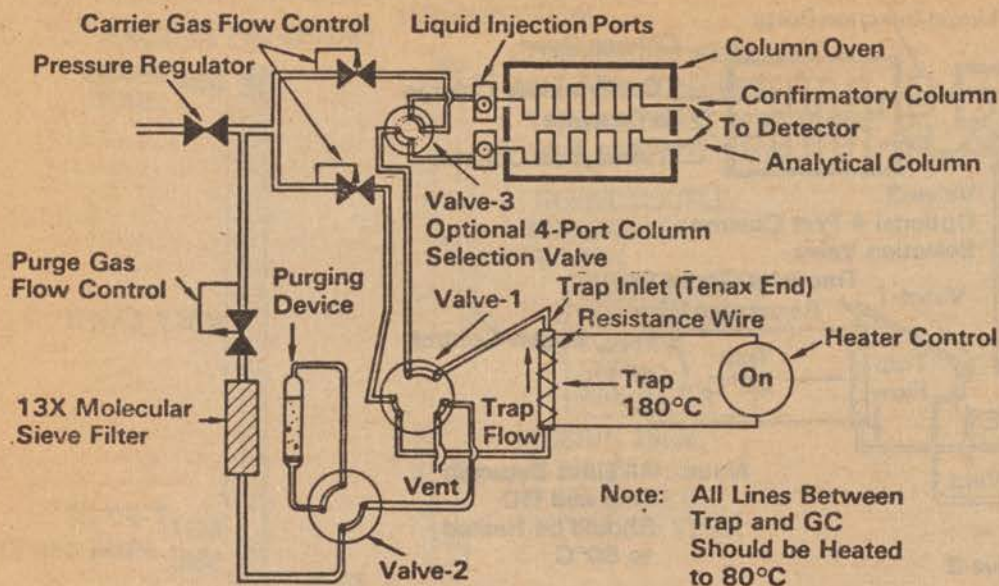


Figure 5. Purge and trap system-desorb mode.

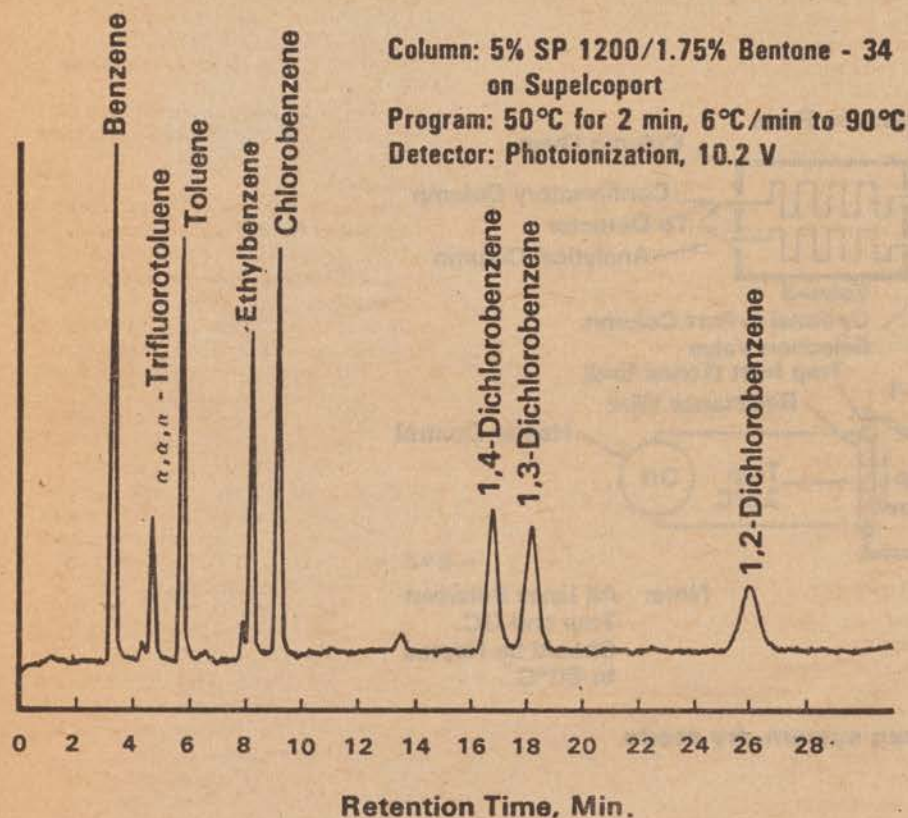


Figure 6. Gas chromatogram of purgeable aromatics.

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Method 603—Acrolein and Acrylonitrile

1. Scope and Application

1.1 This method covers the determination of acrolein and acrylonitrile. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Acrolein	34210	107-02-8
Acrylonitrile	34215	107-13-1

1.2 This is a purge and trap gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for either or both of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 624 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for the parameters listed above, if used with the purge and trap conditions described in this method.

1.3 The method detection limit (MDL, defined in Section 12.1) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the analytes are trapped. After the purge is completed, the trap is heated and backflushed with the inert gas to desorb the compound onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the analytes which are then detected with a flame ionization detector.^{2,3}

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences that may occur.

3. Interferences

3.1 Impurities in the purge gas and organic compound outgassing from the plumbing of the trap account for the majority

of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high analyte levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105 °C between analyses. The trap and other parts of the system are also subject to contamination, therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this view point, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{4,5} for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: a purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column

at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device must be capable of being heated to 85 °C within 3.0 min after transfer of the sample to the purging device and being held at 85 ± 2 °C during the purge cycle. The entire water column in the purging device must be heated. Design of this modification to the standard purging device is optional, however, use of a water bath is suggested.

5.2.1.1 Heating mantle—To be used to heat water bath.

5.2.1.2 Temperature controller—Equipped with thermocouple/sensor to accurately control water bath temperature to ± 2 °C. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain 1.0 cm of methyl silicone coated packing (Section 6.5.2) and 23 cm of 2,6-diphenylene oxide polymer (Section 6.5.1). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber must be capable of rapidly heating the trap to 180 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit as illustrated in Figure 3 or be coupled to a gas chromatograph.

5.3 pH paper—Narrow pH range, about 3.5 to 5.5 (Fisher Scientific Short Range Alkacid No. 2, #14-837-2 or equivalent).

5.4 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.4.1 Column 1—10 ft long x 2 mm ID glass or stainless steel, packed with Porapak-QS (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 12. Guidelines for the use of alternate column packings are provided in Section 10.1.

5.4.2 Column 2—6 ft long x 0.1 in. ID glass or stainless steel, packed with Chromosorb 101 (60/80 mesh) or equivalent.

5.4.3 Detector—Flame ionization detector. This type of detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 12. Guidelines for the use of alternate detectors are provided in Section 10.1.

5.5 Syringes—5-mL, glass hypodermic with Luerlok tip (two each).

5.6 Micro syringes—25-μL, 0.006 in. ID needle.

5.7 Syringe valve—2-way, with Luer ends (three each).

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrisorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.4 Hydrochloric acid (1+1)—Slowly, add 50 mL of concentrated HCl (ACS) to 50 mL of reagent water.

6.5 Trap Materials:

6.5.1 2,6-Diphenylene oxide polymer—Tenax (60/80 mesh), chromatographic grade or equivalent.

6.5.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.6 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in reagent water using assayed liquids. Since acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.6.1 Place about 9.8 mL of reagent water into a 10-mL ground glass stoppered volumetric flask. For acrolein standards the reagent water must be adjusted to pH 4 to 5. Weight the flask to the nearest 0.1 mg.

6.6.2 Using a 100-μL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the water without contacting the neck of the flask.

6.6.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Optionally, stock standard solutions may be prepared using the pure standard material by volumetrically measuring the appropriate amounts and determining the weight of the material using the density of the material. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.6.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4 °C and protect from light.

6.6.5 Prepare fresh standards daily.

6.7 Secondary dilution standards—Using stock standard solutions, prepare secondary dilution standards in reagent water that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3.1 or 7.4.1 will bracket the working range of the analytical system. Secondary dilution standards should be prepared daily and stored at 4 °C.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1. Calibrate the purge and trap-gas chromatographic system using either the external standard technique (Section 7.3) or the internal standard technique (Section 7.4).

7.3 External standard calibration procedure:

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μL of one or more secondary dilution standards to 100, 500, or 1000 mL of reagent water. A 25-μL syringe with a 0.006 in. ID needle should be used for this operation. One of the external standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These standards must be prepared fresh daily.

7.3.2 Analyze each calibration standard according to Section 10, and tabulate peak height or area responses versus the concentration of the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.4 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.4.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.3.1.

7.4.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.6 and 6.7. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μg/mL of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μg/L.

7.4.3 Analyze each calibration standard according to Section 10, adding 10 μL of internal standard spiking solution directly to the syringe (Section 10.4). Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.5 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of a QC check sample.

7.5.1 Prepare the QC check sample as described in Section 8.2.2.

7.5.2 Analyze the QC check sample according to Section 10.

7.5.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 2. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, a new calibration curve, calibration factor, or RF must be prepared for that parameter according to Section 7.3 or 7.4.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check

standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 25 µg/mL in reagent water. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 50 µg/L of each parameter by adding 200 µL of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and

analysis of actual samples can begin. If either s exceeds the precision limit or either $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for each compound of interest.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 50 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 µL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed. NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 10 µL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of

each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (S_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁸ Field test kits are available for this purpose.

9.2 If acrolein is to be analyzed, collect about 500 mL of sample in a clean glass container. Adjust the pH of the sample to 4 to 5 using acid or base, measuring with narrow range pH paper. Samples for acrolein analysis receiving no pH adjustment must be analyzed within 3 days of sampling.

9.3 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative

has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

9.4 All samples must be analyzed within 14 days of collection.³

10. Procedure

10.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are estimated retention times and MDL that can be achieved under these conditions. An example of the separations achieved by Column 1 is shown in Figure 5. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

10.2 Calibrate the system daily as described in Section 7.

10.3 Adjust the purge gas (nitrogen or helium) flow rate to 20 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

10.4 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 µL of the internal standard spiking solution (Section 7.4.2), if applicable, through the valve bore then close the valve.

10.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

10.6 Close both valves and purge the sample for 15.0 ± 0.1 min while heating at 85 ± 2 °C.

10.7 After the 15-min purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180 °C while backflushing the trap with an inert gas between 20 and 60 mL/min for 1.5 min.

10.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

10.9 After desorbing the sample for 1.5 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 210 °C. After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

10.10 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11. Calculations

11.1 Determine the concentration of individual compounds in the sample.

11.1.1 If the external standard calibration procedure is used, calculate the concentration of the parameter being measured from the peak response using the calibration curve or calibration factor determined in Section 7.3.2.

11.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.4.3 and Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(RF)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard.

11.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

12. Method Performance

12.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.⁴ The MDL concentrations listed in Table 1 were obtained using reagent water.⁵ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

12.2 This method is recommended for the concentration range from the MDL to 1,000×MDL. Direct aqueous injection techniques should be used to measure concentration levels above 1,000×MDL.

12.3 In a single laboratory (Battelle-Columbus), the average recoveries and standard deviations presented in Table 2 were obtained.⁶ Seven replicate samples were analyzed at each spike level.

References

- 40 CFR Part 136, Appendix B.
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- "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
- "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
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- "Evaluation of Method 803," Final report for EPA Contract 68-03-1760 (In preparation).

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

Column 1 conditions: Porapak-QS (60/100 mesh) packed in a 10 ft × 2 mm ID glass or stainless steel column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 110 °C for 1.5 min (during desorption), then heated as rapidly as possible to 150 °C and held for 20 min; column bakeout at 190 °C for 10 min.⁸

Column 2 conditions: Chromosorb 101 (60/80 mesh) packed in a 6 ft × 0.1 in. ID glass or stainless steel column with helium carrier gas at 40 mL/min flow rate. Column temperature held isothermal at 80 °C for 4 min, then programmed at 50 °C/min to 120 °C and held for 12 min.

TABLE 2.—SINGLE LABORATORY ACCURACY AND PRECISION—METHOD 603

Parameter	Sample matrix	Spike conc. (µg/L)	Average recovery (µg/L)	Standard deviation (µg/L)	Average percent recovery
Acrolein	RW	5.0	5.2	0.2	104
	RW	50.0	51.4	0.7	103
	POTW	5.0	4.0	0.2	80
	POTW	50.0	44.4	0.8	89
	IW	5.0	0.1	0.1	2
	IW	100.0	9.3	1.1	9
Acrylonitrile	RW	5.0	4.2	0.2	84
	RW	50.0	51.4	1.5	103
	POTW	20.0	20.1	0.8	100
	POTW	100.0	101.3	1.5	101
	IW	10.0	9.1	0.8	91
	IW	100.0	104.0	3.2	104

RW=Reagent water.

POTW=Prechlorination secondary effluent from a municipal sewage treatment plant.

IW=Industrial wastewater containing an unidentified acrolein reactant.

TABLE 3.—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 603 *

Parameter	Range for Q (µg/L)	Limit for S (µg/L)	Range for X (µg/L)	Range for P, P _s (%)
Acrolein	45.9-54.1	4.6	42.9-60.1	88-118
Acrylonitrile	41.2-58.8	9.9	33.1-69.9	71-135

Q=Concentration measured in QC check sample, in µg/L (Section 7.5.3).

S=Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

X=Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s=Percent recovery measured (Section 8.3.2, Section 8.4.2).

—Criteria were calculated assuming a QC check sample concentration of 50 µg/L.

BILLING CODE 6560-50-M

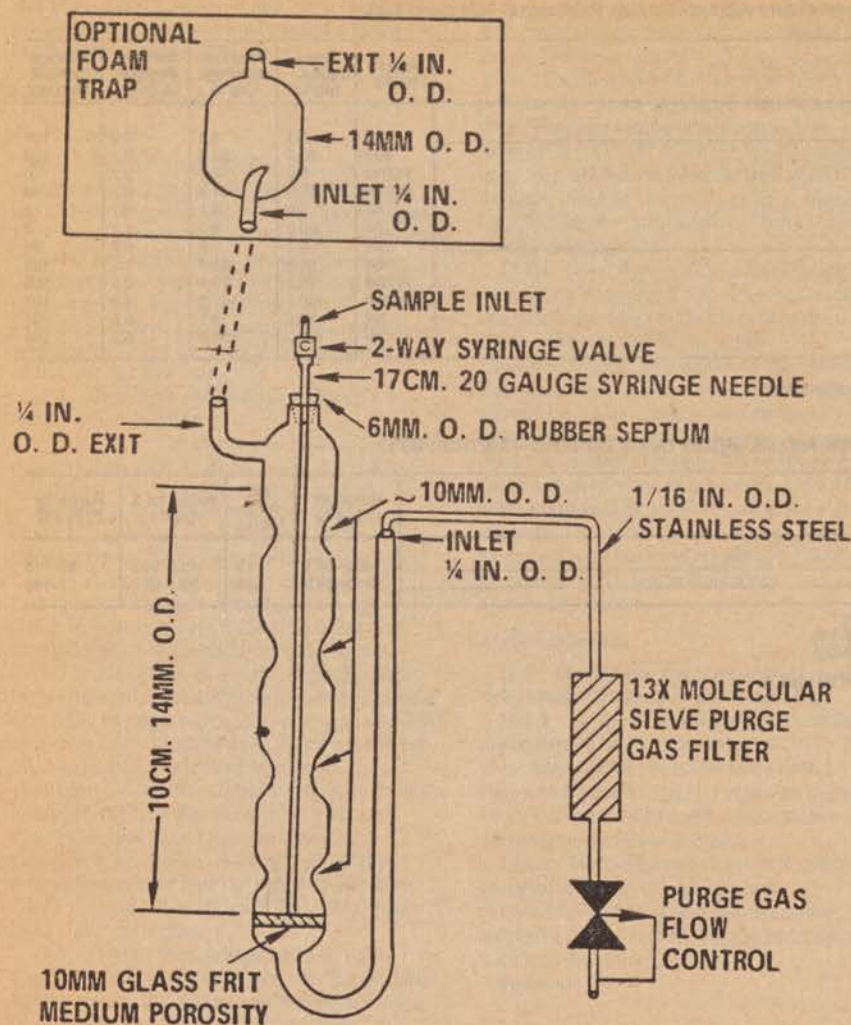


Figure 1. Purging device.

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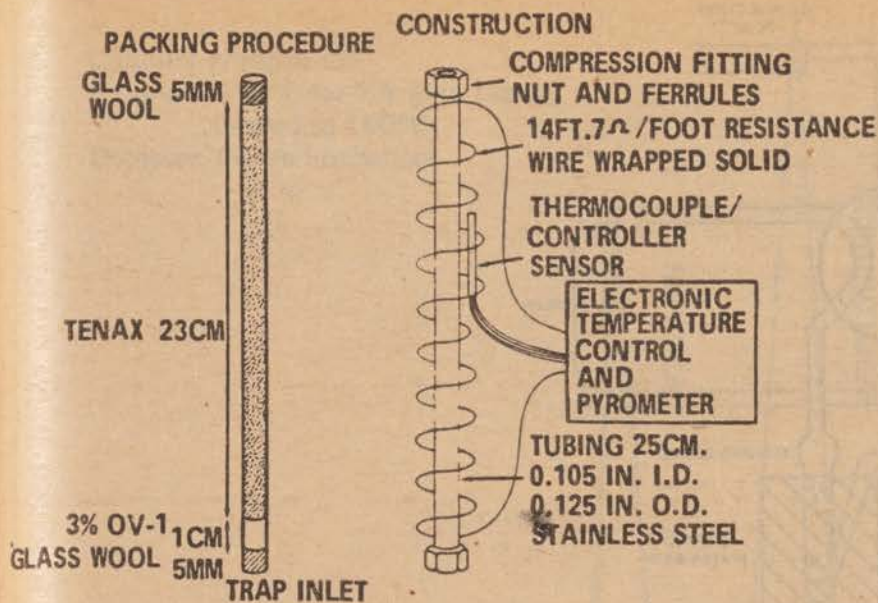


Figure 2. Trap packings and construction to include desorb capability.

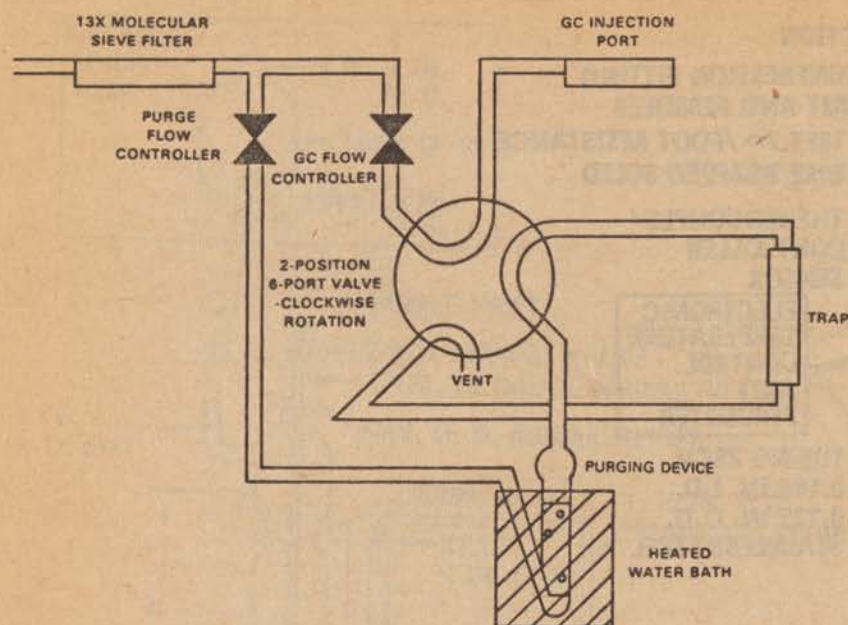


Figure 3. Purge and trap system-purge mode.

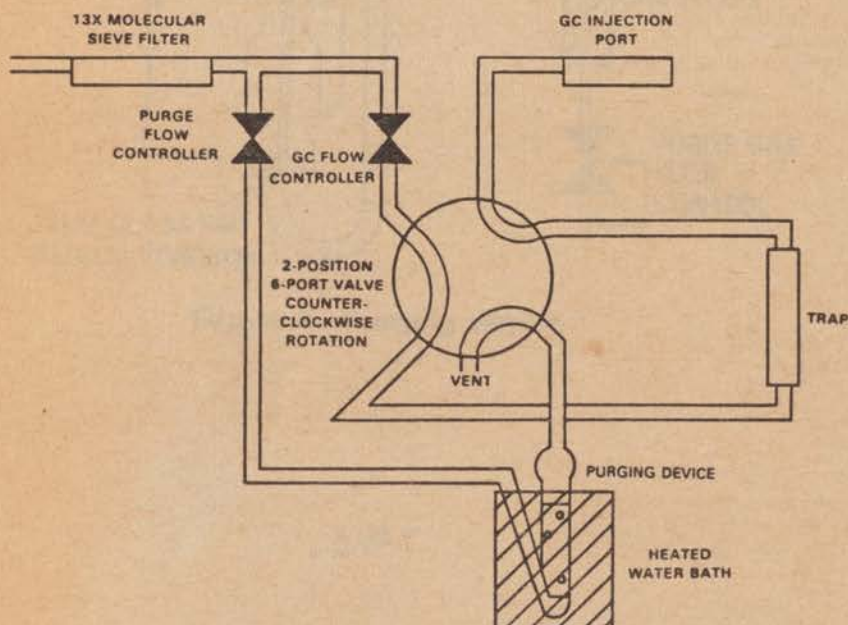


Figure 4. Purge and trap system-desorb mode.

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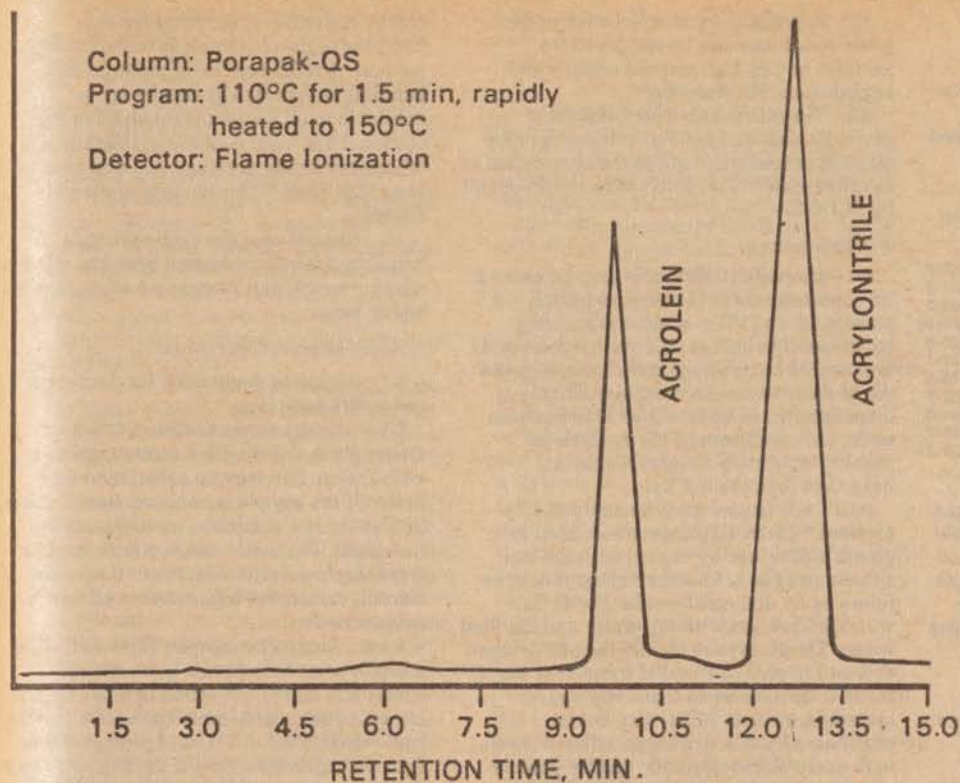


Figure 5. Gas chromatogram of acrolein and acrylonitrile.

BILLING CODE 6560-50-C

Method 604—Phenols

1. Scope and Application

1.1 This method covers the determination of phenol and certain substituted phenols. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34646	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2

1.2 This is a flame ionization detector gas chromatographic (FIDGC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for derivatization, cleanup, and electron capture detector gas chromatography (ECDGC) that can be used to confirm measurements made by FIDGC. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix. The MDL listed in Table 1 for each parameter was achieved with a flame ionization detector (FID). Comparable results were achieved when the derivatization cleanup and electron capture detector (ECD) were employed (Table 2).

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is acidified and extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to 2-propanol during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the phenols are then measured with an FID.²

2.2 A preliminary sample wash under basic conditions can be employed for samples having high general organic and organic base interferences.

2.3 The method also provides for a derivatization and column chromatography cleanup procedure to aid in the elimination of interferences.^{2,3} The derivatives are analyzed by ECDGC.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.⁴ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The derivatization cleanup procedure in Section 12 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Tables 1 and 2.

3.3 The basic sample wash (Section 10.2) may cause significantly reduced recovery of phenol and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of

OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified⁵⁻⁷ for the information of analyst.

4.2 Special care should be taken in handling pentafluorobenzyl bromide, which is a lachrymator, and 18-crown-6-ether, which is highly toxic.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 400 mm long x 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—100 mm long x 10 mm ID, with Teflon stopcock.

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.8 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.9 Reaction flask—15 to 25-mL round bottom flask, with standard tapered joint, fitted with a water-cooled condenser and U-shaped drying tube containing granular calcium chloride.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column for underivatized phenols—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

5.6.2 Column for derivatized phenols—1.8 m long x 2 mm ID glass, packed with 5% OV-17 on Chromosorb W-AW-DMCS (80/100 mesh) or equivalent. This column has proven effective in the analysis of wastewaters for derivatization products of the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

5.6.3 Detectors—Flame ionization and electron capture detectors. The FID issued when determining the parent phenols. The ECD is used when determining the derivatized phenols. Guidelines for the use of alternative detectors are provided in Section 11.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium hydroxide solution (1 N)—Dissolve 4 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.4 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.5 Sodium thiosulfate—(ACS) Granular.

6.6 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.7 Sulfuric acid (1 N)—Slowly, add 58 mL of H_2SO_4 (ACS, sp. gr. 1.84) to reagent water and dilute to 1 L.

6.8 Potassium carbonate—(ACS) Powdered.

6.9 Pentafluorobenzyl bromide (α -Bromopentafluorotoluene)—97% minimum purity. Note: This chemical is a lachrymator. (See Section 4.2.)

6.10 18-crown-6-ether (1,4,7,10,13,16-Hexaoxacyclooctadecane)—98% minimum purity. Note: This chemical is highly toxic.

6.11 Derivatization reagent—Add 1 mL of pentafluorobenzyl bromide and 1 g of 18-crown-6-ether to a 50-mL volumetric flask and dilute to volume with 2-propanol. Prepare

fresh weekly. This operation should be carried out in a hood. Store at 4 °C and protect from light.

6.12 Acetone, hexane, methanol, methylene chloride, 2-propanol, toluene—Pesticide quality or equivalent.

6.13 Silica gel—100/200 mesh, Davison, grade-923 or equivalent. Activate at 130 °C overnight and store in a desiccator.

6.14 Stock standard solutions (1.00 $\mu\text{g}/\mu\text{L}$)—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions.

6.14.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in 2-propanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.14.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.14.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.15 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 To calibrate the FIDGC for the analysis of underivatized phenols, establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure for FIDGC:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with 2-propanol. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 11 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure for FIDGC—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with 2-propanol. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 11 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard ($\mu\text{g}/\text{L}$).

C_s = Concentration of the parameter to be measured ($\mu\text{g}/\text{L}$).

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that compound.

7.5 To calibrate the ECDGC for the analysis of phenol derivatives, establish gas chromatographic operating conditions equivalent to those given in Table 2.

7.5.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with 2-propanol. One of the external standards should be at a concentration near, but above, the MDL (Table 2) and the other concentrations should correspond to the expected range of concentrations found in

real samples or should define the working range of the detector.

7.5.2 Each time samples are to be derivatized, simultaneously treat a 1-mL aliquot of each calibration standard as described in Section 12.

7.5.3 After derivatization, analyze 2 to 5 μ L of each column eluate collected according to the method beginning in Section 12.8 and tabulate peak height or area responses against the calculated equivalent mass of underivatized phenol injected. The results can be used to prepare a calibration curve for each compound.

7.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 11.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality

of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 μ g/mL in 2-propanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 μ g/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in μ g/L, and the standard deviation of the recovery (s) in μ g/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the

sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 μ g/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any, or, if none, (2) the larger of either 5 times higher than the expected background concentration or 100 μ g/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 μ g/L, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy ($\bar{X}$) using the equation in Table 4, substituting the spike concentration (T) for C; (2) calculate overall precision (S) using the equation in Table 4, substituting $\bar{X}$ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}/T) \pm 2.44(100 S/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample

concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_r) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_r) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁹ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.¹⁰ Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 For samples high in organic content, the analyst may solvent wash the sample at basic pH as prescribed in Sections 10.2.1 and 10.2.2 to remove potential method interferences. Prolonged or exhaustive contact with solvent during the wash may result in low recovery of some of the phenols, notably phenol and 2,4-dimethylphenol. For relatively clean samples, the wash should be omitted and the extraction, beginning with Section 10.3, should be followed.

10.2.1 Adjust the pH of the sample to 12.0 or greater with sodium hydroxide solution.

10.2.2 Add 60 mL of methylene chloride to the sample by shaking the funnel for 1 min with periodic venting to release vapor pressure. Discard the solvent layer. The wash can be repeated up to two additional times if significant color is being removed.

10.3 Adjust the sample to a pH of 1 to 2 with sulfuric acid.

10.4 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.5 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded

surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.9 Increase the temperature of the hot water bath to 95 to 100 °C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of 2-propanol. A 5-mL syringe is recommended for this operation. Attach a two-ball micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL of 2-propanol to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 2.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Add an additional 2 mL of 2-propanol through the top of the micro-Snyder column and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.10 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4 °C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with FIDGC analysis (Section 11). If the sample requires further cleanup, proceed to Section 12.

10.11 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Flame Ionization Detector Gas Chromatography

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 1. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

11.2 Calibrate the system daily as described in Section 7.

11.3 If the internal standard calibration procedure is used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

11.4 Inject 2 to 5 μL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.¹¹ Smaller (1.0 μL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL , and the resulting peak size in area or peak height units.

11.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound may be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

11.7 If the measurement of the peak response is prevented by the presence of interferences, an alternative gas chromatographic procedure is required. Section 12 describes a derivatization and column chromatographic procedure which has been tested and found to be a practical means of analyzing phenols in complex extracts.

12. Derivatization and Electron Capture Detector Gas Chromatography

12.1 Pipet a 1.0-mL aliquot of the 2-propanol solution of standard or sample extract into a glass reaction vial. Add 1.0 mL of derivatizing reagent (Section 6.11). This amount of reagent is sufficient to derivatize a solution whose total phenolic content does not exceed 0.3 mg/mL.

12.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

12.3 Cap the mixture and heat it for 4 h at 80 °C in a hot water bath.

12.4 Remove the solution from the hot water bath and allow it to cool.

12.5 Add 10 mL of hexane to the reaction flask and shake vigorously for 1 min. Add 3.0 mL of distilled, deionized water to the reaction flask and shake for 2 min. Decant a portion of the organic layer into a concentrator tube and cap with a glass stopper.

12.6 Place 4.0 g of silica gel into a chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top.

12.7 Preelute the column with 6 mL of hexane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2.0 mL of the hexane solution (Section 12.5) that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate. Elute the column, in order, with: 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 2. Fractions may be

combined as desired, depending upon the specific phenols of interest or level of interferences.

12.8 Analyze the fractions by ECDGC. Table 2 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 2.

12.9 Calibrate the system daily with a minimum of three aliquots of calibration standards, containing each of the phenols of interest that are derivatized according to Section 7.5.

12.10 Inject 2 to 5 μL of the column fractions into the gas chromatograph using the solvent-flush technique. Smaller (1.0 μL) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μL , and the resulting peak size in area or peak height units. If the peak response exceeds the linear range of the system, dilute the extract and reanalyze.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample analyzed by FIDGC (without derivatization) as indicated below.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_1)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (μL).

V₁ = Volume of total extract (μL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted (L).

13.2 Determine the concentration of individual compounds in the sample analyzed by derivatization and ECDGC according to Equation 4.

Equation 4.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)(B)(D)}{(V_1)(V_s)(C)(E)}$$

where:

A = Mass of underivatized phenol represented by area of peak in sample chromatogram, determined from calibration curve in Section 7.5.3 (ng).

V_i = Volume of eluate injected (μL).

V₁ = Total volume of column eluate or combined fractions from which V_i was taken (μL).

V_s = Volume of water extracted in Section 10.10 (mL).

B = Total volume of hexane added in Section 12.5 (mL).

C = Volume of hexane sample solution added to cleanup column in Section 12.7 (mL).

D = Total volume of 2-propanol extract prior to derivatization (mL).

E = Volume of 2-propanol extract carried through derivatization in Section 12.1 (mL).

13.3 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Tables 1 and 2 were obtained using reagent water.¹² Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked as six concentrations over the range 12 to 450 $\mu\text{g/L}$.¹³ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

References

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Method detection limit (µg/L)
2-Chlorophenol.....	1.70	0.31
2-Nitrophenol.....	2.00	0.45
Phenol.....	3.01	0.14
2,4-Dimethylphenol.....	4.03	0.32
2,4-Dichlorophenol.....	4.30	0.39
2,4,6-Trichlorophenol.....	6.05	0.64
4-Chloro-3-methylphenol.....	7.50	0.36
2,4-Dinitrophenol.....	10.00	13.0
2-Methyl-4,6-dinitrophenol.....	10.24	16.0
Pentachlorophenol.....	12.42	7.4
4-Nitrophenol.....	24.25	2.8

Column conditions: Supelcoport (80/100 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2 mm ID glass column with nitrogen carrier gas at 30 mL/min flow rate. Column temperature was 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature. MDL were determined with an FID.

TABLE 2.—SILICA GEL FRACTIONATION AND ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFBB DERIVATIVES

Parent compound	Percent recovery by fraction *				Retention time (min)	Method detection limit (µg/L)
	1	2	3	4		
2-Chlorophenol.....		90	1		3.3	0.58
2-Nitrophenol.....			9	90	9.1	0.77
Phenol.....		90	10		1.8	2.2
2,4-Dimethylphenol.....		95	7		2.9	0.63
2,4-Dichlorophenol.....		95	1		5.8	0.69
2,4,6-Trichlorophenol.....	50	50			7.0	0.58
4-Chloro-3-methylphenol.....		84	14		4.8	1.8
Pentachlorophenol.....	75	20			28.8	0.59
4-Nitrophenol.....			1	90	14.0	0.70

Column conditions: Chromosorb W-AW-DMCS (80/100 mesh) coated with 5% OV-17 packed in a 1.8 m long x 2.0 mm ID glass column with 5% methane/95% argon carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 200 °C. MDL were determined with an ECD.

* Eluant composition:

- Fraction 1—15% toluene in hexane.
- Fraction 2—40% toluene in hexane.
- Fraction 3—75% toluene in hexane.
- Fraction 4—15% 2-propanol in toluene.

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 604

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P _u (percent)
4-Chloro-3-methylphenol.....	100	16.6	56.7-113.4	99-122
2-Chlorophenol.....	100	27.0	54.1-110.2	38-126
2,4-Dichlorophenol.....	100	25.1	59.7-103.3	44-119
2,4-Dimethylphenol.....	100	33.3	50.4-100.0	24-118
4,6-Dinitro-2-methylphenol.....	100	25.0	42.4-123.6	30-136
2,4-Dinitrophenol.....	100	36.0	31.7-125.1	12-145
2-Nitrophenol.....	100	22.5	56.6-103.8	43-117
4-Nitrophenol.....	100	19.0	22.7-100.0	13-110
Pentachlorophenol.....	100	32.4	56.7-113.5	36-134
Phenol.....	100	14.1	32.4-100.0	23-108
2,4,6-Trichlorophenol.....	100	16.6	60.8-110.4	53-119

s—Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

$\bar{X}$ —Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_u—Percent recovery measured (Section 8.3.2, Section 8.4.2).

NOTE.—These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 604

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single Analyst precision, s_x ($\mu\text{g/L}$)	Overall precision, S ($\mu\text{g/L}$)
4-Chloro-3-methylphenol	0.87C-1.97	0.11 $\bar{X}$ -0.21	0.16 $\bar{X}$ +1.41
2-Chlorophenol	0.83C-0.84	0.18 $\bar{X}$ +0.20	0.21 $\bar{X}$ +0.75
2,4-Dichlorophenol	0.81C+0.48	0.17 $\bar{X}$ -0.02	0.18 $\bar{X}$ +0.62
2,4-Dimethylphenol	0.62C-1.64	0.30 $\bar{X}$ -0.69	0.25 $\bar{X}$ +0.48
4,6-Dinitro-2-methylphenol	0.84C-1.01	0.15 $\bar{X}$ +1.25	0.19 $\bar{X}$ +5.85
2,4-Dinitrophenol	0.80C-1.58	0.27 $\bar{X}$ -1.15	0.29 $\bar{X}$ +4.51
2-Nitrophenol	0.81C-0.76	0.15 $\bar{X}$ +0.44	0.14 $\bar{X}$ +3.84
4-Nitrophenol	0.46C+0.18	0.17 $\bar{X}$ +2.43	0.19 $\bar{X}$ +4.79
Pentachlorophenol	0.83C+2.07	0.22 $\bar{X}$ -0.58	0.23 $\bar{X}$ +0.57
Phenol	0.43C+0.11	0.20 $\bar{X}$ -0.88	0.17 $\bar{X}$ +0.77
2,4,6-Trichlorophenol	0.86C-0.40	0.10 $\bar{X}$ +0.53	0.13 $\bar{X}$ +2.40

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_x = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

BILLING CODE 6560-50-M

COLUMN: 1% SP-1240DA ON SUPELCOPORT
PROGRAM: 80°C AT INJECTION, IMMEDIATE 8°C/MIN TO 150°C
DETECTOR: FLAME IONIZATION

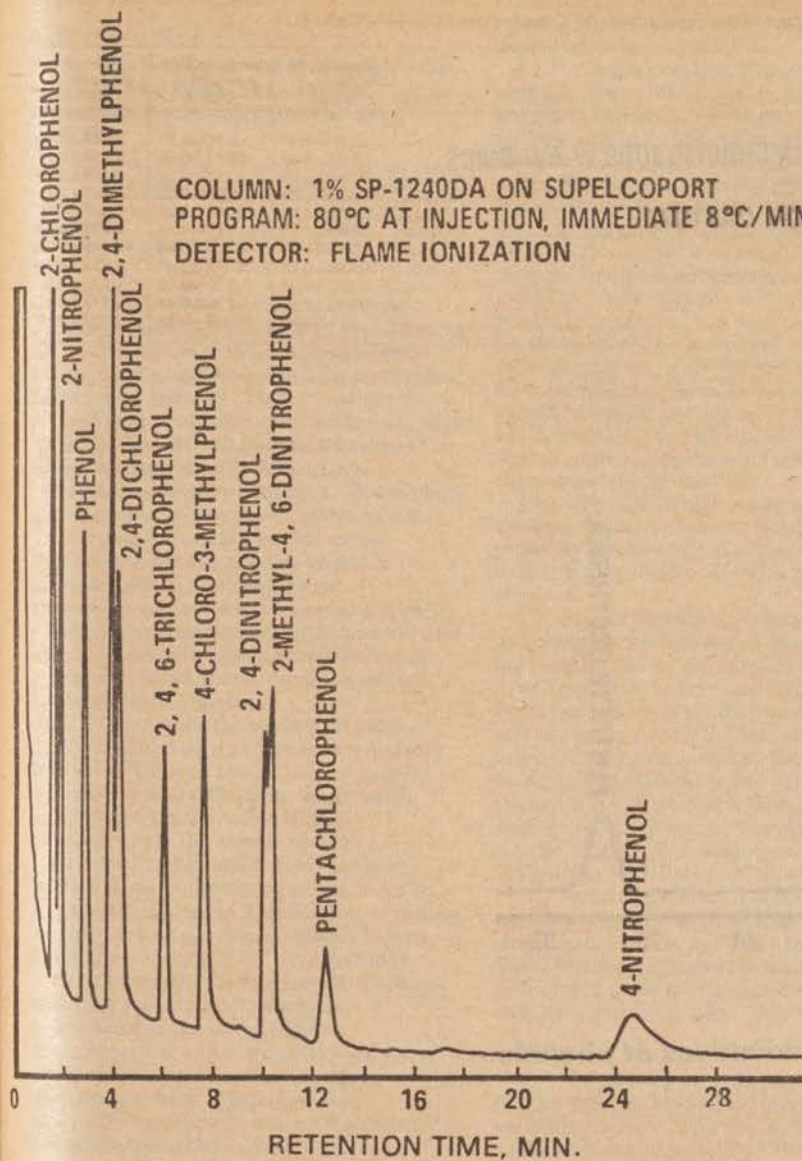


Figure 1. Gas chromatogram of phenols.

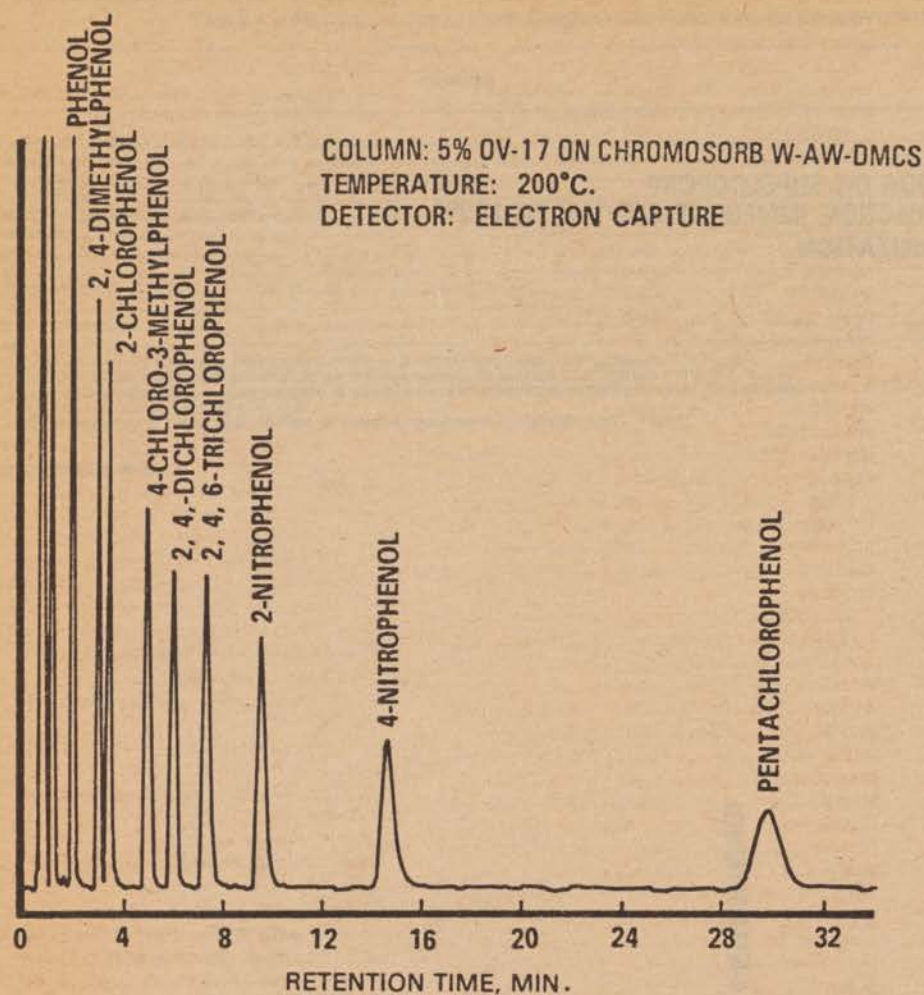


Figure 2. Gas chromatogram of PFB derivatives of phenols.

BILLING CODE 6560-50-C

Method 605—Benzidines**1. Scope and Application**

1.1 This method covers the determination of certain benzidines. The following parameters can be determined by this method:

Parameter	Storet No.	CAS No.
Benzidine.....	39120	92-87-5
3,3'-Dichlorobenzidine.....	34631	91-84-1

1.2 This is a high performance liquid chromatography (HPLC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for the compounds above, identifications should be supported by at least one additional qualitative technique. This method describes electrochemical conditions at a second potential which can be used to confirm measurements made with this method. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1) ¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of the interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC instrumentation and in the interpretation of liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with chloroform using liquid-liquid extractions in a separatory funnel. The chloroform extract is extracted with acid. The acid extract is then neutralized and extracted with chloroform. The final chloroform extract is exchanged to methanol while being concentrated using a rotary evaporator. The extract is mixed with buffer and separated by HPLC. The benzidine compounds are measured with an electrochemical detector.²

2.2 The acid back-extraction acts as a general purpose cleanup to aid in the elimination of interferences.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in chromatograms. All of these materials must be routinely demonstrated to be free from interferences

under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures that are inherent in the extraction step are used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Some dye plant effluents contain large amounts of components with retention times closed to benzidine. In these cases, it has been found useful to reduce the electrode potential in order to eliminate interferences and still detect benzidine. (See Section 12.7.)

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ^{4,5} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzidine and 3,3'-dichlorobenzidine. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

4.3 Exposure to chloroform should be minimized by performing all extractions and

extract concentrations in a hood or other well-ventilated area.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested):

5.2.1 Separatory funnels—2000, 1000, and 250-mL, with Teflon stopcock.

5.2.2 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.3 Rotary evaporator.

5.2.4 Flasks—Round bottom, 100-mL, with 24/40 joints.

5.2.5 Centrifuge tubes—Conical, graduated, with Teflon-lined screw caps.

5.2.6 Pipettes—Pasteur, with bulbs.

5.3 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.4 High performance liquid chromatography (HPLC)—An analytical system complete with column supplies, high pressure syringes, detector, and compatible recorder. A data system is recommended for measuring peak areas and retention times.

5.4.1 Solvent delivery system—With pulse damper, Altex 110A or equivalent.

5.4.2 Injection valve (optional)—Waters U6K or equivalent.

5.4.3 Electrochemical detector—Bioanalytical Systems LC-2A with glassy carbon electrode, or equivalent. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

5.4.4 Electrode polishing kit—Princeton Applied Research Model 9320 or equivalent.

5.4.5 Column—Lichrosorb RP-2, 5 micron particle diameter, in a 25 cm × 4.6 mm ID stainless steel column. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is

not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (5 N)—Dissolve 20 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium hydroxide solution (1 M)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 1 L.

6.4 Sodium thiosulfate—(ACS) Granular.

6.5 Sodium tribasic phosphate (0.4 M)—Dissolve 160 g of trisodium phosphate decahydrate (ACS) in reagent water and dilute to 1 L.

6.6 Sulfuric acid (1+1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.7 Sulfuric acid (1 M)—Slowly, add 58 mL of H₂SO₄ (ACS, sp. gr. 1.84) to reagent water and dilute to 1 L.

6.8 Acetate buffer (0.1 M, pH 4.7)—Dissolve 5.8 mL of glacial acetic acid (ACS) and 13.6 g of sodium acetate trihydrate (ACS) in reagent water which has been purified by filtration through a RO-4 Millipore System or equivalent and dilute to 1 L.

6.9 Acetonitrile, chloroform (preserved with 1% ethanol), methanol—Pesticide quality or equivalent.

6.10 Mobile phase—Place equal volumes of filtered acetonitrile (Millipore type FH filter or equivalent) and filtered acetate buffer (Millipore type GS filter or equivalent) in a narrow-mouth, glass container and mix thoroughly. Prepare fresh weekly. Degas daily by sonicating under vacuum, by heating and stirring, or by purging with helium.

6.11 Stock standard solutions (1.00 µg/µL)—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish chromatographic operating conditions equivalent to those given in Table 1. The HPLC system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with mobile phase. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using syringe injections of 5 to 25 µL or a constant volume injection loop, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with mobile phase. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using syringe injections of 5 to 25 µL or a constant volume injection loop, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF

can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that compound. If serious loss of response occurs, polish the electrode and recalibrate.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.9, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality

of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing benzidine and/or 3,3'-dichlorobenzidine at a concentration of 50 µg/mL each in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 50 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 50 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if

none (2) the larger of either 5 times higher than the expected background concentration or 50 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than 50 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$.⁷

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and

corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as HPLC with a dissimilar column, gas chromatography, or mass spectrometry must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁸ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4°C and stored in the dark from the time of collection until extraction. Both benzidine and 3,3'-dichlorobenzidine are easily oxidized. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁹ Field test kits are available for this purpose. After mixing, adjust the pH of the sample to a range of 2 to 7 with sulfuric acid.

9.3 If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

9.4 All samples must be extracted within 7 days of collection. Extracts may be held up to 7 days before analysis, if stored under an inert (oxidant free) atmosphere.² The extract should be protected from light.

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust

to within the range of 6.5 to 7.5 with sodium hydroxide solution or sulfuric acid.

10.2 Add 100 mL of chloroform to the sample bottle, seal, and shake 30 s to rinse the inner surface. (Caution: Handle chloroform in a well ventilated area.) Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the chloroform extract in a 250-mL separatory funnel.

10.3 Add a 50-mL volume of chloroform to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the separatory funnel. Perform a third extraction in the same manner.

10.4 Separate and discard any aqueous layer remaining in the 250-mL separatory funnel after combining the organic extracts. Add 25 mL of 1 M sulfuric acid and extract the sample by shaking the funnel for 2 min. Transfer the aqueous layer to a 250-mL beaker. Extract with two additional 25-mL portions of 1 M sulfuric acid and combine the acid extracts in the beaker.

10.5 Place a stirbar in the 250-mL beaker and stir the acid extract while carefully adding 5 mL of 0.4 M sodium tribasic phosphate. While monitoring with a pH meter, neutralize the extract to a pH between 6 and 7 by dropwise addition of 5 N sodium hydroxide solution while stirring the solution vigorously. Approximately 25 to 30 mL of 5 N sodium hydroxide solution will be required and it should be added over at least a 2-min period. Do not allow the sample pH to exceed 8.

10.6 Transfer the neutralized extract into a 250-mL separatory funnel. Add 30 mL of chloroform and shake the funnel for 2 min. Allow the phases to separate, and transfer the organic layer to a second 250-mL separatory funnel.

10.7 Extract the aqueous layer with two additional 20-mL aliquots of chloroform as before. Combine the extracts in the 250-mL separatory funnel.

10.8 Add 20 mL of reagent water to the combined organic layers and shake for 30 s.

10.9 Transfer the organic extract into a 100-mL round bottom flask. Add 20 mL of methanol and concentrate to 5 mL with a rotary evaporator at reduced pressure and 35 °C. An aspirator is recommended for use as the source of vacuum. Chill the receiver with ice. This operation requires approximately 10 min. Other concentration techniques may be used if the requirements of Section 8.2 are met.

10.10 Using a 9-in. Pasteur pipette, transfer the extract to a 15-mL, conical, screw-cap centrifuge tube. Rinse the flask, including the entire side wall, with 2-mL portions of methanol and combine with the original extract.

10.11 Carefully concentrate the extract to 0.5 mL using a gentle stream of nitrogen while

heating in a 30 °C water bath. Dilute to 2 mL with methanol, reconcentrate to 1 mL, and dilute to 5 mL with acetate buffer. Mix the extract thoroughly. Cap the centrifuge tube and store refrigerated and protected from light if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with HPLC analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.12 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure.

12. High Performance Liquid Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the HPLC. Included in this table are retention times, capacity factors, and MDL that can be achieved under these conditions. An example of the separations achieved by this HPLC column is shown in Figure 1. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met. When the HPLC is idle, it is advisable to maintain a 0.1 mL/min flow through the column to prolong column life.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the instrument.

12.4 Inject 5 to 25 µL of the sample extract or standard into the HPLC. If constant volume injection loops are not used, record the volume injected to the nearest 0.05 µL, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract with mobile phase and reanalyze.

12.7 If the measurement of the peak response for benzidine is prevented by the presence of interferences, reduce the electrode potential to +0.6 V and reanalyze.

If the benzidine peak is still obscured by interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_e)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_e = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_i)(\text{RF})(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_i = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_o = Volume of water extracted (L).

13.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹⁰ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 7 × MDL to 3000 × MDL.¹⁰

14.3 This method was tested by 17 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 70 µg/L.¹¹ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample

matrix. Linear equations to describe these relationships are presented in Table 3.

References

1. 40 CFR Part 136, Appendix B.
2. "Determination of Benzidines in Industrial and Municipal Wastewaters," EPA-600/4-82-022, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, May 1982.
3. ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
4. "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health

Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)
8. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for

Sampling Water," American Society for Testing and Materials, Philadelphia.

9. "Methods 330.4 (Titrimetric, DPD-FAS) and 330.5 (Spectrophotometric, DPD) for Chlorine Total Residual," Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.
10. "Determination of Method Detection Limit and Analytical Curve by EPA Method 605—Benzidines," Special letter report for EPA Contract 68-03-2624, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
11. "EPA Method Validation Study 15, Method 605 (Benzidines)," Report for EPA Contract 68-03-2624 (In preparation).

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Column capacity factor (k')	Method detection limit (µg/L)
Benzidine	6.1	1.44	0.06
3,3'-Dichlorobenzidine	12.1	3.84	0.13

HPLC Column conditions: Lichrosorb RP-2, 5 micron particle size, in a 25 cm x 4.6 mm ID stainless steel column. Mobile Phase: 0.8 mL/min of 50% acetonitrile/50% 0.1M pH 4.7 acetate buffer. The MDL were determined using an electrochemical detector operated at +0.8 V.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 605

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P _s (percent)
Benzidine	50	18.7	9.1-61.0	D-140
3,3'-Dichlorobenzidine	50	23.6	18.7-50.0	5-128

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 605

Parameter	Accuracy, as recovery, $\bar{X}$ (µg/L)	Single analyst precision, s_x (µg/L)	Overall precision, S_x (µg/L)
Benzidine	$0.70C + 0.06$	$0.28\bar{X} + 0.19$	$0.40\bar{X} + 0.18$
3,3'-Dichlorobenzidine	$0.66C + 0.23$	$0.39\bar{X} - 0.05$	$0.38\bar{X} + 0.02$

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_x = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.

S_x = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

COLUMN: LICHROSORB RP-2

MOBILE PHASE: 50% ACETONITRILE IN ACETATE BUFFER

DETECTOR: ELECTROCHEMICAL AT + 0.8 V

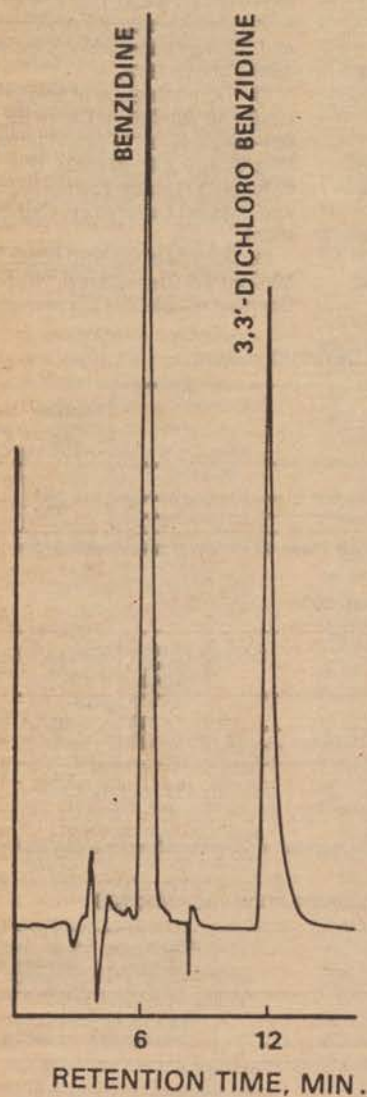


Figure 1. Liquid chromatogram of benzidines.

BILLING CODE 6560-50-C

Method 606—Phthalate Esters

1. Scope and Application

1.1 This method covers the determination of certain phthalate esters. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Bis(2-ethylhexyl) phthalate	39100	117-81-7
Butyl benzyl phthalate	34292	85-68-7
Di-n-butyl phthalate	39110	84-74-2
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
Di-n-octyl phthalate	34596	117-84-0

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 608, 609, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and

exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the phthalate esters are then measured with an electron capture detector.²

2.2 Analysis for phthalates is especially complicated by their ubiquitous occurrence in the environment. The method provides Florisil and alumina column cleanup procedures to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Phthalate esters are contaminants in many products commonly found in the laboratory. It is particularly important to avoid the use of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination can result at any time, if consistent quality control is not practiced. Great care must be experienced to prevent such contamination. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.^{4,5}

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified⁶⁻⁸ for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only).

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long × 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—300 mm long × 10 mm ID, with Teflon stopcock and coarse frit filter disc at bottom (Kontes K-420540-0213 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.8 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long $\times$ 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long $\times$ 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Acetone, hexane, isooctane, methylene chloride, methanol—Pesticide quality or equivalent.

6.3 Ethyl ether—nanograde, redistilled in glass if necessary.

6.3.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.3.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.4 Sodium sulfate—(ACS) Granular, anhydrous. Several levels of purification may be required in order to reduce background phthalate levels to an acceptable level: 1) Heat 4 h at 400 °C in a shallow tray, 2) Heat 16 h at 450 to 500 °C in a shallow tray, 3) Soxhlet extract with methylene chloride for 48 h.

6.5 Florisil—PR grade (60/100 mesh). Purchase activated at 1250 °F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 h at 40 °C. After heating transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 h. Keep the bottle sealed tightly.

6.6 Alumina—Neutral activity Super I, W200 series (ICN Life Sciences Group, No. 404583). To prepare for use, place 100 g of alumina into a 500-mL beaker and heat for approximately 16 h at 400 °C. After heating transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 h. Keep the bottle sealed tightly.

6.7 Stock standard solutions (1.00 μ g/ μ L)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatograph operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepared calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μ L, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range ($< 10\%$ relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μ L, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (μ g/L).

C_s = Concentration of the parameter to be measured (μ g/L).

If the RF value over the working range is a constant ($< 10\%$ RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that compound.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality

checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at the following concentrations in acetone: butyl benzyl phthalate, 10 µg/mL; bis(2-ethylhexyl)phthalate, 50 µg/mL; di-n-octyl phthalate, 50 µg/mL; any other phthalate, 25 µg/mL. The QC check sample concentrate must be obtained from the U.S.

Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 2 by adding 1.00 mL of QC check

sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's

spike to background ratio approaches 5:1.⁹ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most

productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹⁰ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min. with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentrator devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10 mL. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11. Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure.

11.2 If the entire extract is to be cleaned up by one of the following procedures, it must be concentrated to 2.0 mL. To the concentrator tube in Section 10.8, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on a hot water bath (80 °C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the

concentrator tube with 0.2 mL of hexane. Adjust the final volume to 2.0 mL and proceed with one of the following cleanup procedures.

11.3 Florisil column cleanup for phthalate esters:

11.3.1 Place 10 g of Florisil into a chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

11.3.2 Preequilibrate the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

11.3.3 Next, elute the column with 100 mL of 20% ethyl ether in hexane (V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction as in Section 10.6. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to 10 mL in the concentrator tube and analyze by gas chromatography (Section 12).

11.4 Alumina column cleanup for phthalate esters:

11.4.1 Place 10 g of alumina into a chromatographic column. Tap the column to settle the alumina and add 1 cm of anhydrous sodium sulfate to the top.

11.4.2 Preequilibrate the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

11.4.3 Next, elute the column with 140 mL of 20% ethyl ether in hexane (V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction as in Section 10.6. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to 10 mL in the concentrator tube and analyze by gas chromatography (Section 12).

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 and 2. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and

mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 μ L of the sample extract or standard into the gas-chromatograph using the solvent-flush technique.¹¹ Smaller (1.0 μ L) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_s)(V_e)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (μ L).

V_s = Volume of total extract (μ L).

V_e = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_e)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (μ g).

V_e = Volume of water extracted (L).

13.2 Report results in μ g/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹² Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from $5 \times \text{MDL}$ to $1000 \times \text{MDL}$ with the following exceptions: dimethyl and diethyl phthalate recoveries at $1000 \times \text{MDL}$ were low (70%); bis-2-ethylhexyl and di-n-octyl phthalate recoveries at $5 \times \text{MDL}$ were low (60%).¹²

14.3 This method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.7 to 106 μ g/L.¹³ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (μ g/L)
	Column 1	Column 2	
Dimethyl phthalate	2.03	0.95	0.29
Diethyl phthalate	2.82	1.27	0.49
Di-n-butyl phthalate	8.65	3.50	0.36
Butyl benzyl phthalate	* 6.94	* 5.11	0.34
Bis(2-ethylhexyl) phthalate	* 8.92	* 10.5	2.0
Di-n-octyl phthalate	* 16.2	* 18.0	3.0

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m long $\times$ 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 180°C, except where otherwise indicated.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV-1 packed in a 1.8 m long $\times$ 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 200°C, except where otherwise indicated.

* 220°C column temperature.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 606

Parameter	Test conc. ($\mu\text{g/L}$)	Limit for s ($\mu\text{g/L}$)	Range for $\bar{X}$ ($\mu\text{g/L}$)	Range for P, P _s (percent)
Bis(2-ethylhexyl) phthalate.....	50	38.4	1.2-55.9	D-158
Butyl benzyl phthalate.....	10	4.2	5.7-11.0	30-136
Di-n-butyl phthalate.....	25	8.9	10.3-29.6	23-136
Diethyl phthalate.....	25	9.0	1.9-33.4	D-149
Dimethyl phthalate.....	25	9.5	1.3-35.5	D-156
Di-n-octyl phthalate.....	50	13.4	D-50.0	D-114

s = Standard deviation of four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 606

Parameter	Accuracy, as recovery, $\bar{X}'$ ($\mu\text{g/L}$)	Single analyst precision, s_s' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Bis(2-ethylhexyl) phthalate.....	$0.53C + 2.02$	$0.80\bar{X} - 2.56$	$0.73\bar{X} - 0.17$
Butyl benzyl phthalate.....	$0.82C + 0.13$	$0.26\bar{X} + 0.04$	$0.25\bar{X} + 0.07$
Di-n-butyl phthalate.....	$0.79C + 0.17$	$0.23\bar{X} + 0.20$	$0.29\bar{X} + 0.06$
Diethyl phthalate.....	$0.70C + 0.13$	$0.27\bar{X} + 0.05$	$0.45\bar{X} + 0.11$
Dimethyl phthalate.....	$0.73C + 0.17$	$0.26\bar{X} + 0.14$	$0.44\bar{X} + 0.31$
Di-n-octyl phthalate.....	$0.35C - 0.71$	$0.38\bar{X} + 0.71$	$0.62\bar{X} + 0.34$

$\bar{X}'$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_s' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

BILLING CODE 6560-50-M

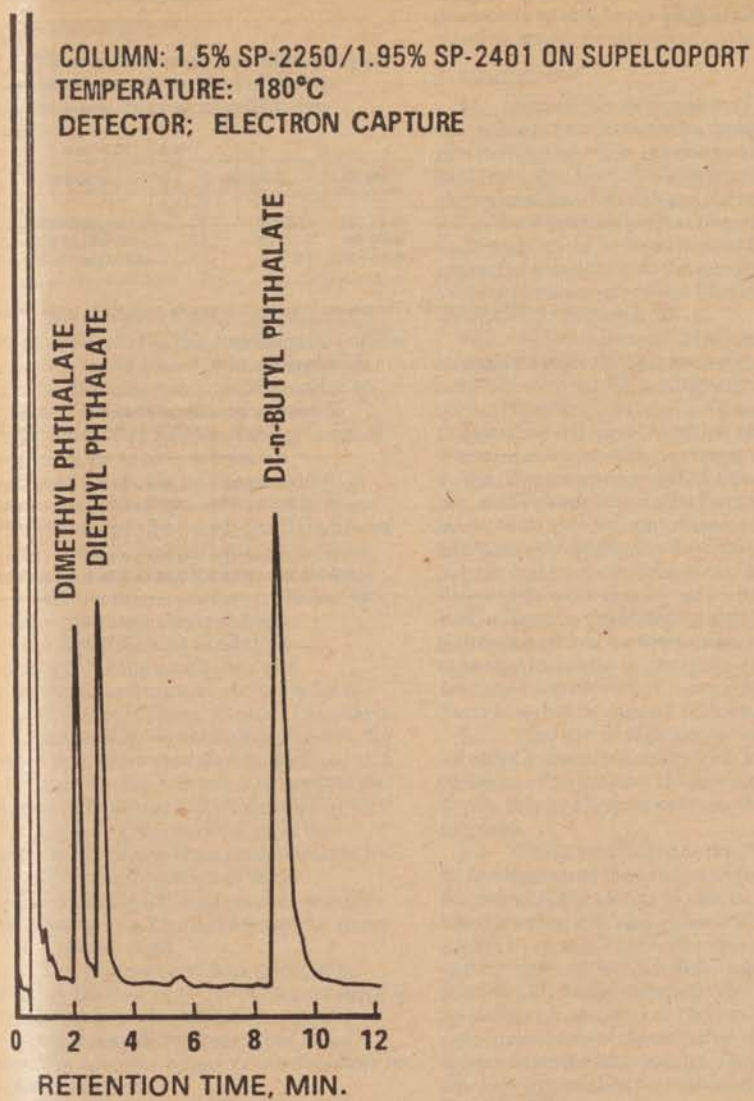


Figure 1. Gas chromatogram of phthalates.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPFICOPORT

TEMPERATURE: 220°C

DETECTOR: ELECTRON CAPTURE

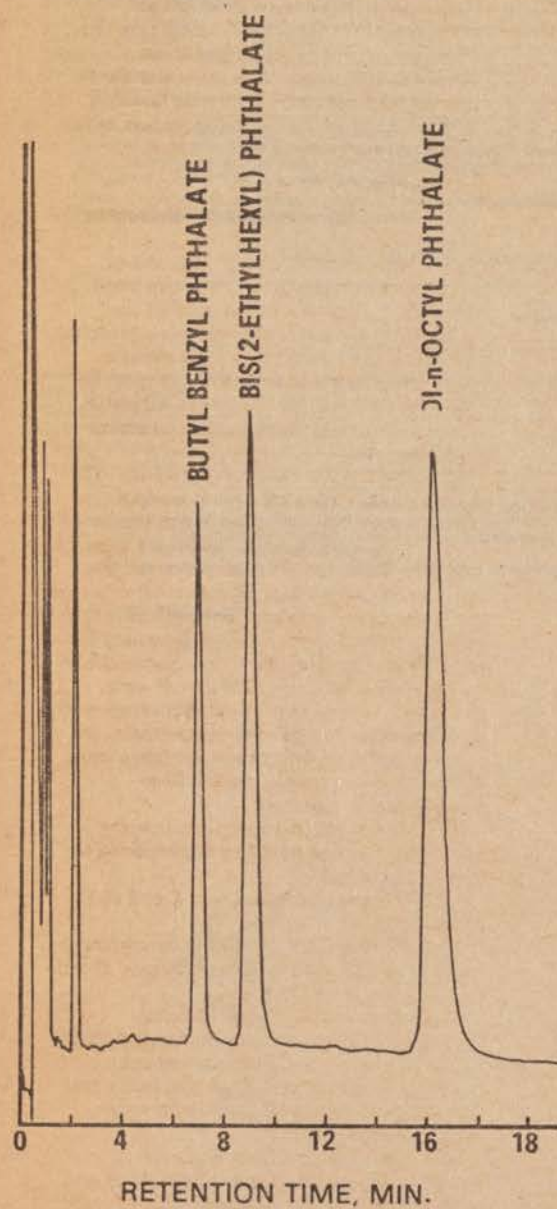


Figure 2. Gas chromatogram of phthalates.

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Method 607—Nitrosamines

1. Scope and Application

1.1 This method covers the determination of certain nitrosamines. The following parameters can be determined by this method:

Parameter	Storet No.	CAS No.
N-Nitrosodimethylamine	34438	62-75-9
N-Nitrosodiphenylamine	34433	86-30-6
N-Nitrosodi-n-propylamine	34428	621-64-7

1.2 This is a gas chromatographic (GC) method applicable to the determination of the parameters listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for N-nitrosodi-n-propylamine. In order to confirm the presence of N-nitrosodiphenylamine, the cleanup procedure specified in Sections 11.3 or 11.4 must be used. In order to confirm the presence of N-nitrosodimethylamine by GC/MS, Column 1 of this method must be substituted for the column recommended in Method 625. Confirmation of these parameters using GC-high resolution mass spectrometry or a Thermal Energy Analyzer is also recommended.^{1,2}

1.3 The method detection limit (MDL, defined in Section 14.1)³ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is washed with dilute hydrochloric acid to remove free amines, dried, and concentrated to a volume of 10 mL or less. After the extract has been exchanged to methanol, it is separated by gas chromatography and the parameters are then measured with a nitrogen-phosphorus detector.⁴

2.2 The method provides Florisil and alumina column cleanup procedures to

separate diphenylamine from the nitrosamines and to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.⁵ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 N-Nitrosodiphenylamine is reported^{6,7} to undergo transnitrosation reactions. Care must be exercised in the heating or concentrating of solutions containing this compound in the presence of reactive amines.

3.4 The sensitive and selective Thermal Energy Analyzer and the reductive Hall detector may be used in place of the nitrogen-phosphorus detector when interferences are encountered. The Thermal Energy Analyzer offers the highest selectivity of the non-MS detectors.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made

available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{10,12} for the information of the analyst.

4.2 These nitrosamines are known carcinogens¹³⁻¹⁷, therefore, utmost care must be exercised in the handling of these materials. Nitrosamine reference standards and standard solutions should be handled and prepared in a ventilated glove box within a properly ventilated room.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flowmeter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnels—2-L and 250-mL, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long × 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Chromatographic column—Approximately 400 mm long × 22 mm ID, with Teflon stopcock and coarse frit filter disc at bottom (Kontes K-420540-0234 or equivalent), for use in Florisil column cleanup procedure.

5.2.9 Chromatographic column—Approximately 300 mm long × 10 mm ID, with Teflon stopcock and coarse frit filter

disc at bottom (Kontes K-420540-0213 or equivalent), for use in alumina column cleanup procedure.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long $\times$ 4 mm ID glass, packed with 10% Carbowax 20 M/2% KOH on Chromosorb W-AW (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.2.

5.6.2 Column 2—1.8 m long $\times$ 4 mm ID glass, packed with 10% SP-2250 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Nitrogen-phosphorus, reductive Hall, or Thermal Energy Analyzer detector.^{1,2} These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1). A nitrogen-phosphorus detector was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.2.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.6 Hydrochloric acid (1+9)—Add one volume of concentrated HCl (ACS) to nine volumes of reagent water.

6.7 Acetone, methanol, methylene chloride, pentane—Pesticide quality or equivalent.

6.8 Ethyl ether—Nanograde, redistilled in glass if necessary.

6.8.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat No. P1126-8, and other suppliers.)

6.8.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.9 Florisil—PR grade (60/100 mesh). Purchase activated at 1250 °F and store in the dark in glass containers with ground glass

stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130 °C in a foil-covered glass container and allow to cool.

6.10 Alumina—Basic activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To prepare for use, place 100 g of alumina into a 500-mL reagent bottle and add 2 mL of reagent water. Mix the alumina preparation thoroughly by shaking or rolling for 10 min and let it stand for at least 2 h. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

6.11 Stock standard solutions (1.00 μ g/ μ L)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with methanol. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μ L, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD), linearity through the origin

can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with methanol. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μ L, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (μ g/L).

C_s = Concentration of the parameter to be measured (μ g/L).

If the RF value over the working range is a constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that compound.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and

document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 10.4, 11.1, and 12.2) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 20 µg/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 20 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 20 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.¹⁸ If spiking was performed at a concentration lower than 20 µg/L, the analyst must use

either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$.¹⁸

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note: The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the

environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹⁹ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.²⁰ Field test kits are available for this purpose. If N-nitrosodiphenylamine is to be determined, adjust the sample pH to 7 to 10 with sodium hydroxide solution or sulfuric acid.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.⁴

9.4 Nitrosamines are known to be light sensitive.⁷ Samples should be stored in amber or foil-wrapped bottles in order to minimize photolytic decomposition.

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5 to 9 with sodium hydroxide solution or sulfuric acid.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL

concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Add 10 mL of hydrochloric acid to the combined extracts and shake for 2 min. Allow the layers to separate. Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If N-nitrosodiphenylamine is to be measured by gas chromatography, the analyst must first use a cleanup column to eliminate diphenylamine interference (Section 11). If N-nitrosodiphenylamine is of no interest, the analyst may proceed directly with gas chromatographic analysis (Section 12).

10.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

11.2 If the entire extract is to be cleaned up by one of the following procedures, it must be concentrated to 2.0 mL. To the concentrator tube in Section 10.7, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding

about 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 2.0 mL and proceed with one of the following cleanup procedures.

11.3 Florisil column cleanup for nitrosamines:

11.3.1 Place 22 g of activated Florisil into a 22-mm ID chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

11.3.2 Prewet the column with 40 mL of ethyl ether/pentane (15+85)(V/V). Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

11.3.3 Elute the column with 90 mL of ethyl ether/pentane (15+85)(V/V) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

11.3.4 Next, elute the column with 100 mL of acetone/ethyl ether (5+95)(V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

11.3.5 Add 15 mL of methanol to the collected fraction and concentrate as in Section 10.8, except use pentane to prewet the column and set the water bath at 70 to 75 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze by gas chromatography (Section 12).

11.4 Alumina column cleanup for nitrosamines:

11.4.1 Place 12 g of the alumina preparation (Section 6.10) into a 10-mm ID chromatographic column. Tap the column to settle the alumina and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.4.2 Prewet the column with 10 mL of ethyl ether/pentane (3+7)(V/V). Discard the eluate (about 2 mL) and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2 mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

11.4.3 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (3+7)(V/V). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a 500-mL K-D flask equipped with a 10 mL concentrator tube. This fraction contains N-nitrosodiphenylamine and probably a small amount of N-nitrosodiphenylamine.

11.4.4 Next, elute the column with 60 mL of ethyl ether/pentane (1+1)(V/V), collecting the eluate in a second K-D flask equipped with a 10-mL concentrator tube. Add 15 mL of methanol to the K-D flask. This fraction will contain N-nitrosodimethylamine, most of the N-nitrosodi-n-propylamine and any diphenylamine that is present.

11.4.5 Concentrate both fractions as in Section 10.6, except use pentane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze the fractions by gas chromatography (Section 12).

12. Gas Chromatography

12.1 N-nitrosodiphenylamine completely reacts to form diphenylamine at the normal operating temperatures of a GC injection port (200 to 250 °C). Thus, N-nitrosodiphenylamine is chromatographed and detected as diphenylamine. Accurate determination depends on removal of diphenylamine that may be present in the original extract prior to GC analysis (See Section 11).

12.2 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 and 2. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.3 Calibrate the system daily as described in Section 7.

12.4 If the extract has not been subjected to one of the cleanup procedures in Section 11, it is necessary to exchange the solvent from methylene chloride to methanol before the thermionic detector can be used. To a 1 to 10-mL volume of methylene chloride extract in a concentrator tube, add 2 mL of methanol and a clean boiling chip. Attach a two-ball micro-Snyder column to the concentrator tube. Prewet the column by adding about 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100 °C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL of methanol. Adjust the final volume to 2.0 mL.

12.5 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.6 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.²¹ Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, and the resulting peak size in area or peak height units.

12.7 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.8 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.9 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_e)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_e = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(\text{RF})(V_e)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_e = Volume of water extracted (L).

13.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above

zero.³ The MDL concentrations listed in Table 1 were obtained using reagent water.²² Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 x MDL to 1000 x MDL.²²

14.3 This method was tested by 17 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.8 to 55 µg/L.²³ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
N-Nitrosodimethylamine	4.1	0.88	0.15
N-Nitrosodi-n-propylamine	12.1	4.2	.46
N-Nitrosodiphenylamine*	* 12.8	* 6.4	.81

Column 1 conditions: Chromosorb W-AW (80/100 mesh) coated with 10% Carbowax 20 M/2% KOH packed in a 1.8 m long x 4 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held isothermal at 110 °C, except where otherwise indicated.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 10% SP-2250 packed in a 1.8 m long x 4 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held isothermal at 120 °C, except where otherwise indicated.

* Measured as diphenylamine.

* 220 °C column temperature.

* 210 °C column temperature.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 607

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for $\bar{X}$ (µg/L)	Range for P, P ₁ (percent)
N-Nitrosodimethylamine	20	3.4	4.6-20.0	13-109
N-Nitrosodiphenyl	20	6.1	2.1-24.5	D-139
N-Nitrosodi-n-propylamine	20	5.7	11.5-26.8	45-146

s = Standard deviation for four recovery measurements, in µg/L (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P₁ = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 607

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s _r (µg/L)	Overall precision, S (µg/L)
N-Nitrosodimethylamine	0.37C + 0.06	0.25 $\bar{X}$ - 0.04	0.25 $\bar{X}$ + 0.11
N-Nitrosodiphenylamine	0.64C + 0.52	0.36 $\bar{X}$ - 1.53	0.46 $\bar{X}$ - 0.47
N-Nitrosodi-n-propylamine	0.86C - 0.07	0.15 $\bar{X}$ + 0.13	0.21 $\bar{X}$ + 0.15

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in µg/L.

s_r = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in µg/L.

C = True value for the concentration, in µg/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

COLUMN: 10% CARBOWAX 20M / 2% KOH ON CHROMOSORB W-AW
TEMPERATURE: 110°C
DETECTOR: PHOSPHORUS/NITROGEN

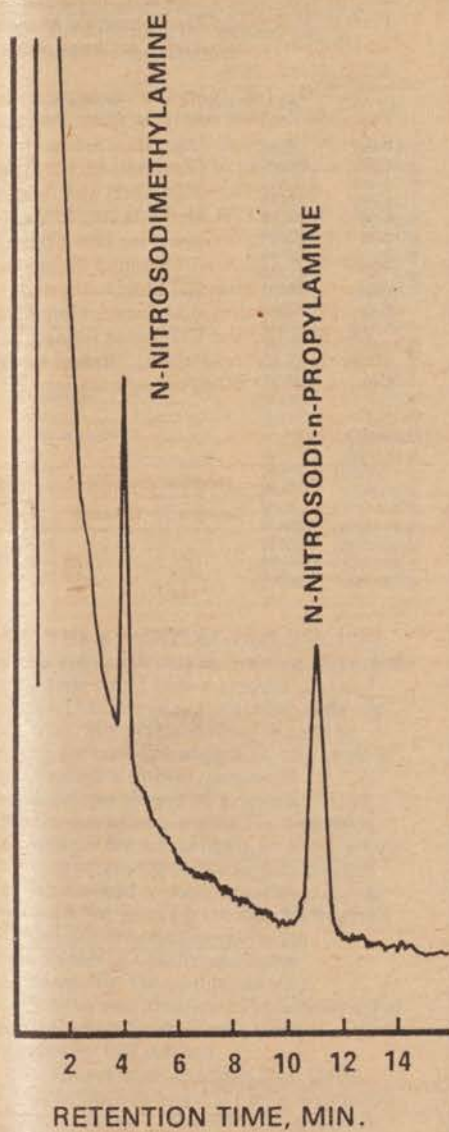


Figure 1. Gas chromatogram of nitrosamines.

COLUMN: 10% CARBOWAX 20M / 2% KOH ON CHROMOSORB W-AW

TEMPERATURE: 220°C

DETECTOR: PHOSPHORUS/NITROGEN

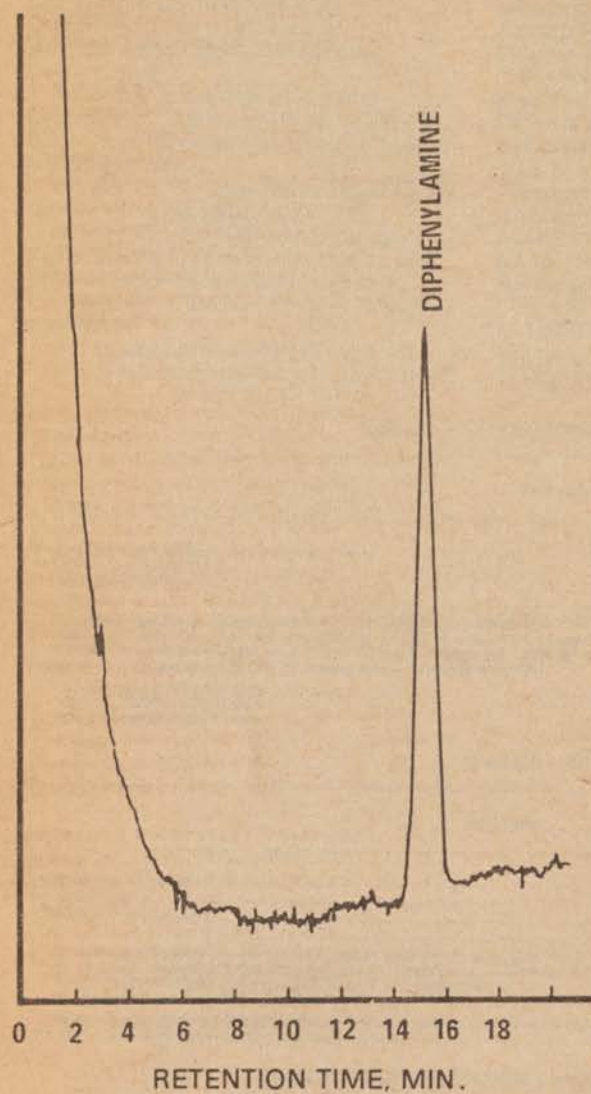


Figure 2. Gas chromatogram of N-nitrosodiphenylamine as diphenylamine.

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Method 608—Organochlorine Pesticides and PCBs**1. Scope and Application**

1.1 This method covers the determination of certain organochlorine pesticides and PCBs. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Aldrin	39330	309-00-2
α -BHC	39337	319-84-6
β -BHC	39338	319-85-7
γ -BHC	34259	319-86-8
δ -BHC	39340	58-99-9
Chlordane	39350	57-74-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dieldrin	39380	60-57-1
Endosulfan I	34361	959-98-8
Endosulfan II	34356	33212-65-9
Endosulfan sulfate	34351	1031-07-8
Endrin	39390	72-20-8
Endrin aldehyde	34366	7421-93-4
Heptachlor	39410	76-44-3
Heptachlor epoxide	39420	1024-57-3
Toxaphene	39400	8001-35-2
PCB-1016	34671	12674-11-2
PCB-1221	39488	1104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-6
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 609, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.²

2.2 The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference.

Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences by phthalate esters can pose a major problem in pesticide analysis when using the electron capture detector. These compounds generally appear in the chromatogram as large late eluting peaks, especially in the 15 and 50% fractions from Florisil. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be

minimized by avoiding the use of plastics in the laboratory. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination.^{4,5} The interferences from phthalate esters can be avoided by using a microcoulometric or electrolytic conductivity detector.

3.3 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{6,7} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: 4,4'-DDT, 4,4'-DDD, the BHCs, and the PCBs. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during composting. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating

flow meter is required to collect flow proportional composites.

5.2. Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long $\times$ 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—400 mm long $\times$ 22 mm ID, with Teflon stopcock and coarse frit filter disc (Kontes K-42054 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna/Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3. Boiling chips—Approximately 10/40 mesh. Heat to 400°C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5. Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6. Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long $\times$ 4 mm ID glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long $\times$ 4 mm ID glass, packed with 3% OV-1 on Supelcoport (100/120 mesh) or equivalent.

5.6.3 Detector—Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL to H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, hexane, isooctane, methylene chloride—Pesticide quality or equivalent.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary.

6.6.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.7 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400°C for 4 h in a shallow tray.

6.8 Florisil—PR grade (60/100 mesh). Purchase activated at 1250°F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130°C in a foil-covered glass container and allow to cool.

6.9 Mercury—Triple distilled.

6.10 Copper powder—Activated.

6.11 Stock standard solutions (1.00 $\mu\text{g}/\mu\text{L}$)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.11.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.11.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.11.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.12 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the

expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range ($<10\%$ relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard ($\mu\text{g}/\text{L}$).

C_s = Concentration of the parameter to be measured ($\mu\text{g}/\text{L}$).

If the RF value over the working range is a constant ($<10\%$ RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, the test must be repeated using a fresh calibration

standard. Alternatively, a new calibration curve must be prepared for that compound.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value⁹ is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

7.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality

of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 µg/mL; 4,4'-DDT, 10 µg/mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; endrin, 10 µg/mL; any other single-component pesticide, 2 µg/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 µg/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/mL; and the standard deviation of the recovery (s) in µg/mL, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from

each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.¹⁰ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy ($\bar{X}$) using the equation in Table 4, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 4, substituting $\bar{X}$ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}'/T) \pm 2.44(100 S'/T)\%$.¹⁰

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC

check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 3 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standards to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_r) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_r) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹¹ should be followed, except that

the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. If the samples will not be extracted within 72 h of collection, the sample should be adjusted to a pH range of 5.0 to 9.0 with sodium hydroxide solution or sulfuric acid. Record the volume of acid or base used. If aldrin is to be determined, add sodium thiosulfate when residual chlorine is present. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.¹² Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus

and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Increase the temperature of the hot water bath to about 80 °C. Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. The Florisil column allows for a select fractionation of the compounds and will eliminate polar interferences. Elemental sulfur, which interferes with the electron capture gas chromatography of certain pesticides, can be removed by the technique described in Section 11.3.

11.2 Florisil column cleanup:

11.2.1 Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 7.5), into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.2 Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate layer to the air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

11.2.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube onto the column. Rinse the tube twice with 1 to 2 mL of hexane, adding each rinse to the column.

11.2.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (V/V) (Fraction 1) at a rate of

about 5 mL/min. Remove the K-D flask and set it aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (V/V) (Fraction 2), into a second K-D flask. Perform the third elution using 200 mL of 50% ethyl ether in hexane (V/V) (Fraction 3). The elution patterns for the pesticides and PCBs are shown in Table 2.

11.2.5 Concentrate the fractions as in Section 10.6, except use hexane to prewet the column and set the water bath at about 85 °C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of each fraction to 10 mL with hexane and analyze by gas chromatography (Section 12).

11.3 Elemental sulfur will usually elute entirely in Fraction 1 of the Florisil column cleanup. To remove sulfur interference from this fraction or the original extract, pipet 1.00 mL of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add one to three drops of mercury and seal.¹³ Agitate the contents of the vial for 15 to 30 s. Prolonged shaking (2 h) may be required. If so, this may be accomplished with a reciprocal shaker. Alternatively, activated copper powder may be used for sulfur removal.¹⁴ Analyze by gas chromatography.

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 to 10. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.¹⁵ Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_t)(V_w)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_t = Volume of total extract (µL).

V_w = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(\text{RF})(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_o = Volume of water extracted (L).

13.2 When it is apparent that two or more PCB (Aroclor) mixtures are present, the Webb and McCall procedure¹⁶ may be used to identify and quantify the Aroclors.

13.3 For multicomponent mixtures (chlordane, toxaphene, and PCBs) match retention times of peaks in the standards with peaks in the sample. Quantitate every identifiable peak unless interference with individual peaks persist after cleanup. Add peak height or peak area of each identified peak in the chromatogram. Calculate as total response in the sample versus total response in the standard.

13.4 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹⁷ Similar results were achieved using

representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4×MDL to 1000×MDL with the following exceptions: Chlordane recovery at 4×MDL was low (60%); Toxaphene recovery was demonstrated linear over the range of 10×MDL to 1000×MDL.¹⁷

14.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations.¹⁸ Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multicomponent parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (μg/L)
	Col. 1	Col. 2	
α-BHC	1.35	1.82	0.003
γ-BHC	1.70	2.13	0.00
β-BHC	1.90	1.97	0.00
Heptachlor	2.00	3.35	0.003
δ-BHC	2.15	2.20	0.009
Aldrin	2.40	4.10	0.004
Heptachlor epoxide	3.50	5.00	0.083
Endosulfan I	4.50	6.20	0.014
4,4'-DDE	5.13	7.15	0.004
Dieldrin	5.45	7.23	0.002
Endrin	6.55	8.10	0.006
4,4'-DDD	7.83	9.08	0.011
Endosulfan II	8.00	8.28	0.004
4,4'-DDT	9.40	11.75	0.012
Endrin aldehyde	11.82	9.30	0.023
Endosulfan sulfate	14.22	10.70	0.066
Chlordane	nr	nr	0.014
Toxaphene	nr	nr	0.24
PCB-1016	nr	nr	nd
PCB-1221	nr	nr	nd
PCB-1232	nr	nr	nd

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS—Continued

Parameter	Retention time (min)		Method detection limit (μg/L)
	Col. 1	Col. 2	
PCB-1242	nr	nr	0.065
PCB-1248	nr	nr	nd
PCB-1254	nr	nr	nd
PCB-1260	nr	nr	nd

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m long x 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 200 °C, except for PCB-1016 through PCB-1248, should be measured at 160 °C.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 3% OV-1 packed in a 1.8 m long x 4 mm ID glass column with 5% methane/95% argon carrier gas at 60 mL/min flow rate. Column temperature held isothermal at 200 °C for the pesticides; at 140 °C for PCB-1221 and 1232; and at 170 °C for PCB-1016 and 1242 to 1260.

nr=Multiple peak response. See Figures 2 thru 10.

nd=Not determined.

TABLE 2.—DISTRIBUTION OF CHLORINATED PESTICIDES AND PCBs INTO FLORISIL COLUMN FRACTIONS²

Parameter	Percent recovery by fraction ^a		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

^a Eluent composition:

Fraction 1—6% ethyl ether in hexane.
Fraction 2—15% ethyl ether in hexane.
Fraction 3—50% ethyl ether in hexane.

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 608

Parameter	Test conc. (μg/L)	Limit for s (μg/L)	Range for X̄ (μg/L)	Range for P _r (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.84	.78-2.80	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 608—Continued

Parameter	Test conc. (μg/L)	Limit for s (μg/L)	Range for X̄ (μg/L)	Range for P _r (%)
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-89.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s=Standard deviation of four recovery measurements, in μg/L (Section 8.2.4).

X̄=Average recovery for four recovery measurements, in μg/L (Section 8.2.4).

P_r=Percent recovery measured (Section 8.3.2, Section 8.4.2).

D=Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 608

Parameter	Accuracy, as recovery, X̄ (μg/L)	Single analyst precision, s _r (μg/L)	Overall precision, S _r (μg/L)
Aldrin	0.81C+0.04	0.16X̄-0.04	0.20X̄-0.01
α-BHC	0.84C+0.03	0.13X̄+0.04	0.23X̄-0.00
β-BHC	0.81C+0.07	0.22X̄-0.02	0.33X̄-0.95
δ-BHC	0.81C+0.07	0.18X̄+0.09	0.25X̄+0.03
γ-BHC	0.82C-0.05	0.12X̄+0.06	0.22X̄+0.04
Chlordane	0.82C-0.04	0.13X̄+0.13	0.18X̄+0.18
4,4'-DDD	0.84C+0.30	0.20X̄-0.18	0.27X̄-0.14
4,4'-DDE	0.85C+0.14	0.13X̄+0.06	0.28X̄-0.09
4,4'-DDT	0.93C-0.13	0.17X̄+0.39	0.31X̄-0.21
Dieldrin	0.90C+0.02	0.12X̄+0.19	0.16X̄+0.16
Endosulfan I	0.97C+0.04	0.10X̄+0.07	0.18X̄+0.08
Endosulfan II	0.93C+0.34	0.41X̄+0.65	0.47X̄-0.20
Endosulfan Sulfate	0.89C-0.37	0.13X̄+0.33	0.24X̄+0.35
Endrin	0.89C-0.04	0.20X̄+0.25	0.24X̄+0.25
Heptachlor	0.69C+0.04	0.06X̄+0.13	0.16X̄+0.08
Heptachlor epoxide	0.89C+0.10	0.16X̄-0.11	0.25X̄-0.08
Toxaphene	0.80C+1.74	0.09X̄+3.20	0.20X̄+0.22
PCB-1016	0.81C+0.50	0.13X̄+0.15	0.15X̄+0.45
PCB-1221	0.96C+0.65	0.29X̄-0.76	0.35X̄-0.62
PCB-1232	0.91C+10.79	0.21X̄-1.93	0.31X̄+3.50
PCB-1242	0.93C+0.70	0.11X̄+1.40	0.21X̄+1.52
PCB-1248	0.97C+1.06	0.17X̄+0.41	0.25X̄-0.37
PCB-1254	0.76C+2.07	0.15X̄+1.66	0.17X̄+3.62
PCB-1260	0.66C+3.76	0.22X̄-2.37	0.39X̄-4.86

X̄=Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_r=Expected single analyst standard deviation of measurements at an average concentration found of X̄, in μg/L.

S_r=Expected interlaboratory standard deviation of measurements at an average concentration found of X̄, in μg/L.

C=True value for the concentration, in μg/L.

X̄=Average recovery found for measurements of samples containing a concentration of C, in μg/L.

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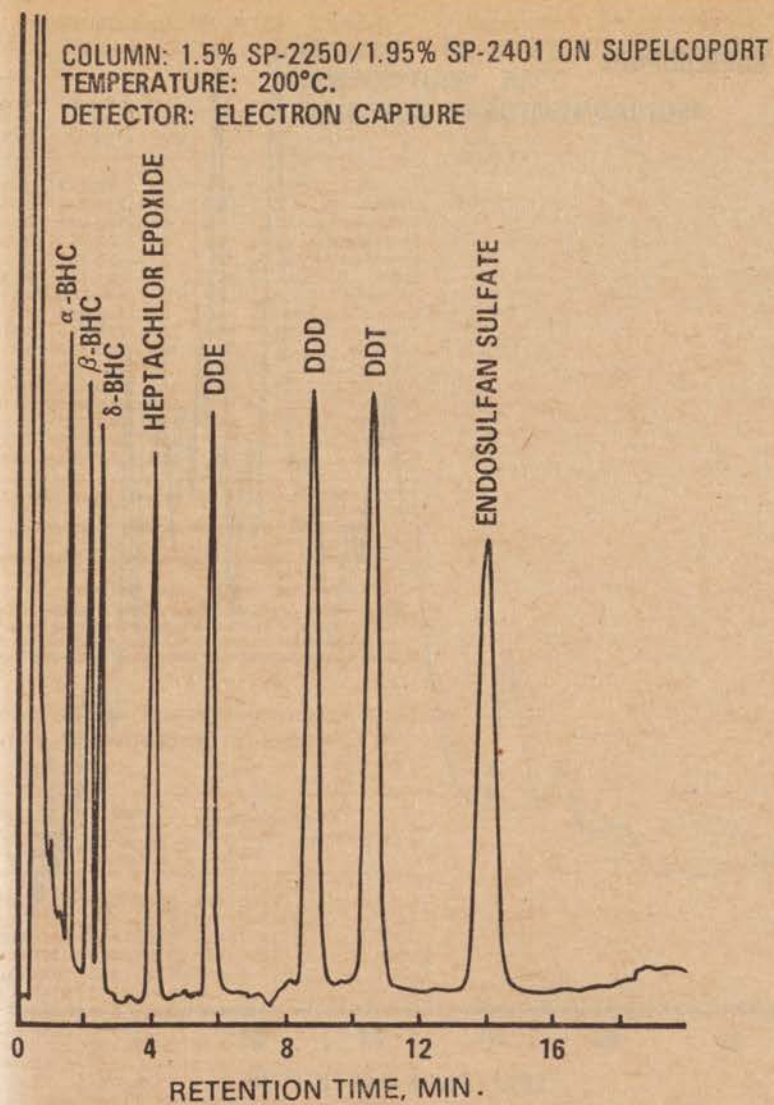


Figure 1. Gas chromatogram of pesticides.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 200°C.
DETECTOR: ELECTRON CAPTURE

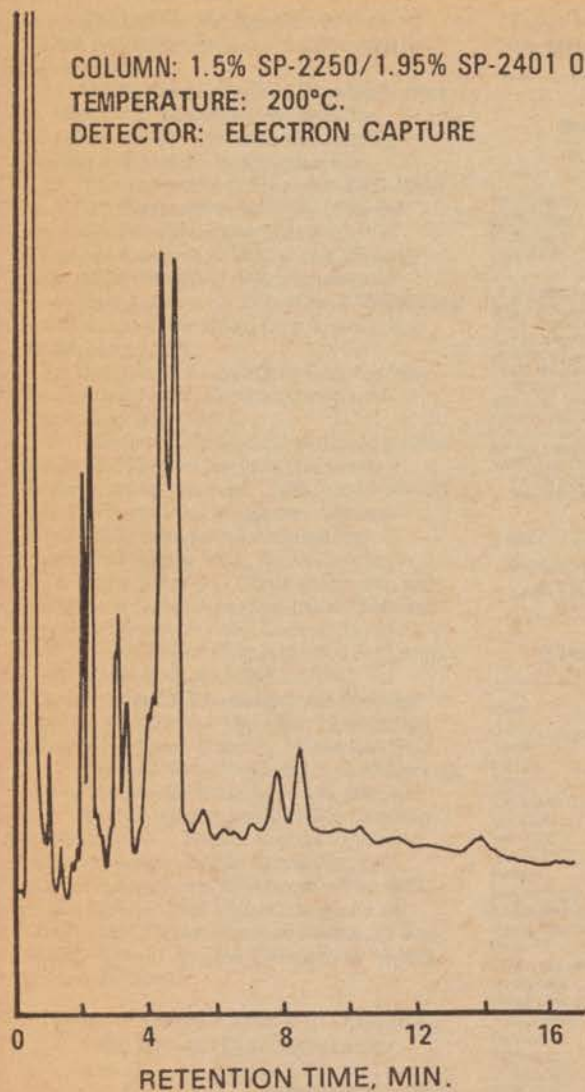


Figure 2. Gas chromatogram of chlordane.

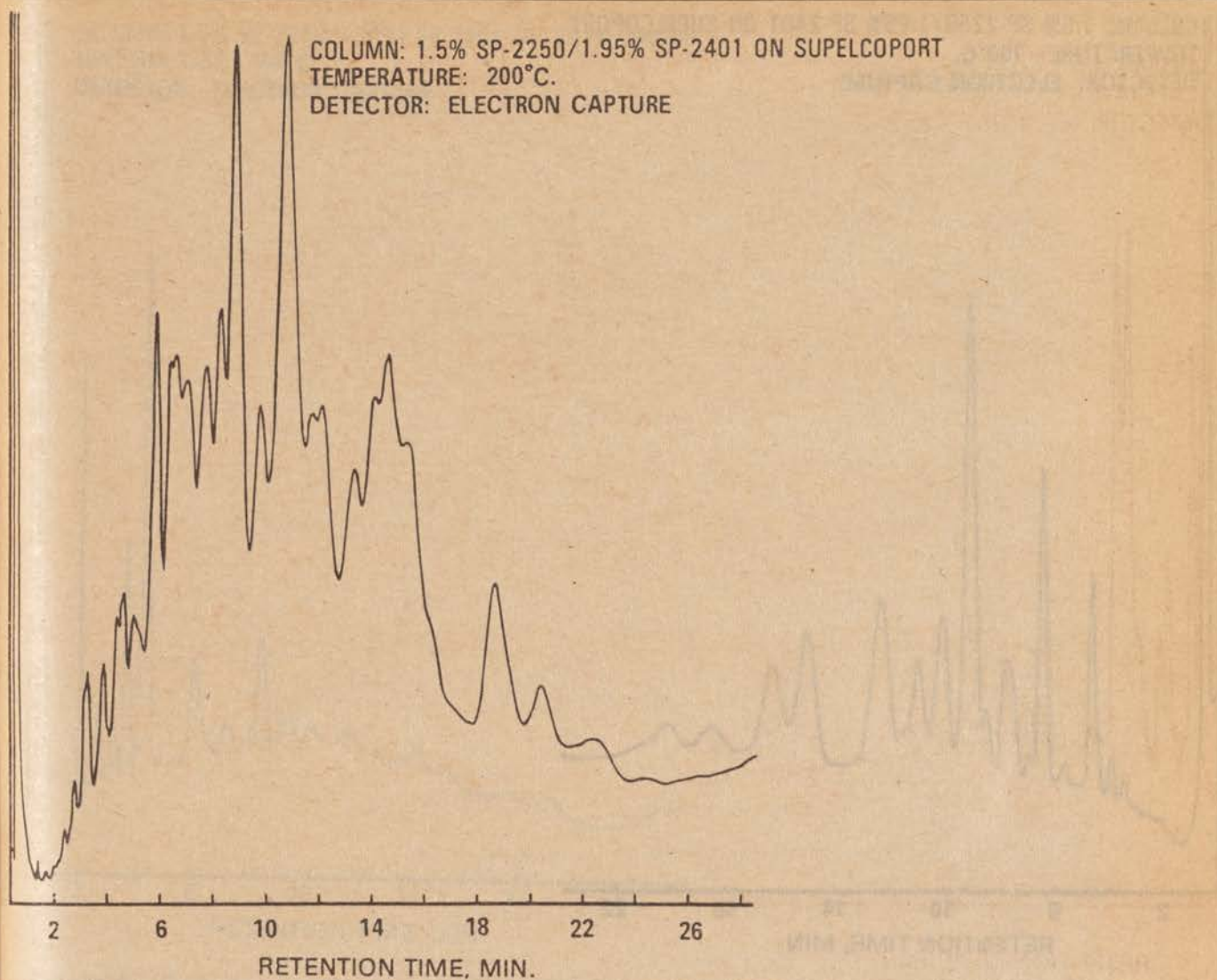


Figure 3. Gas chromatogram of toxaphene.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

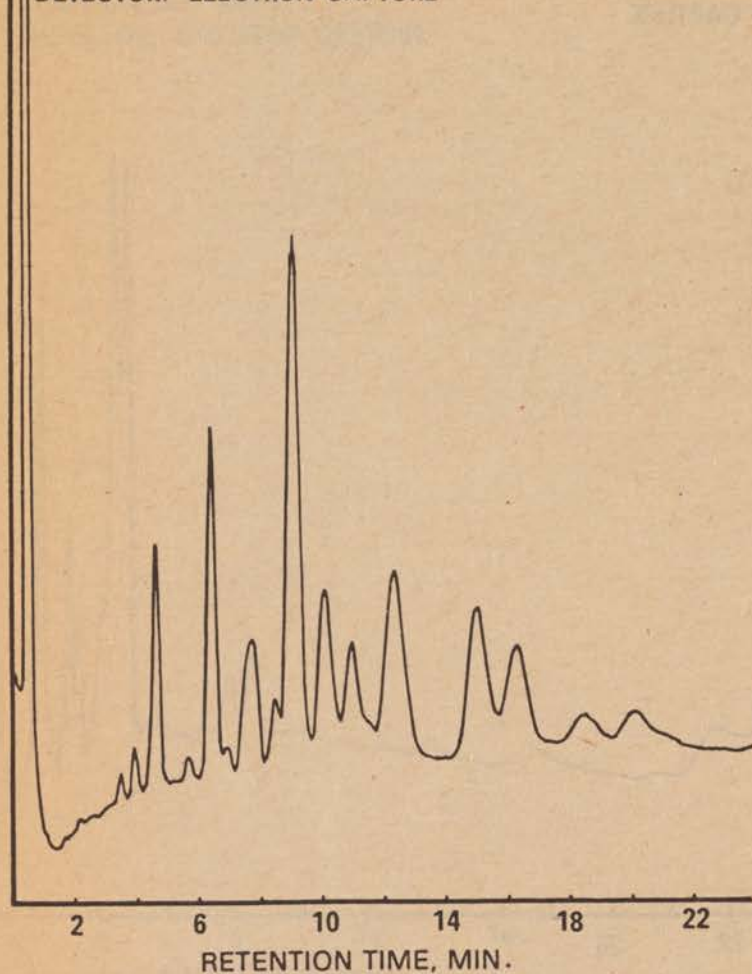


Figure 4. Gas chromatogram of PCB-1016.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

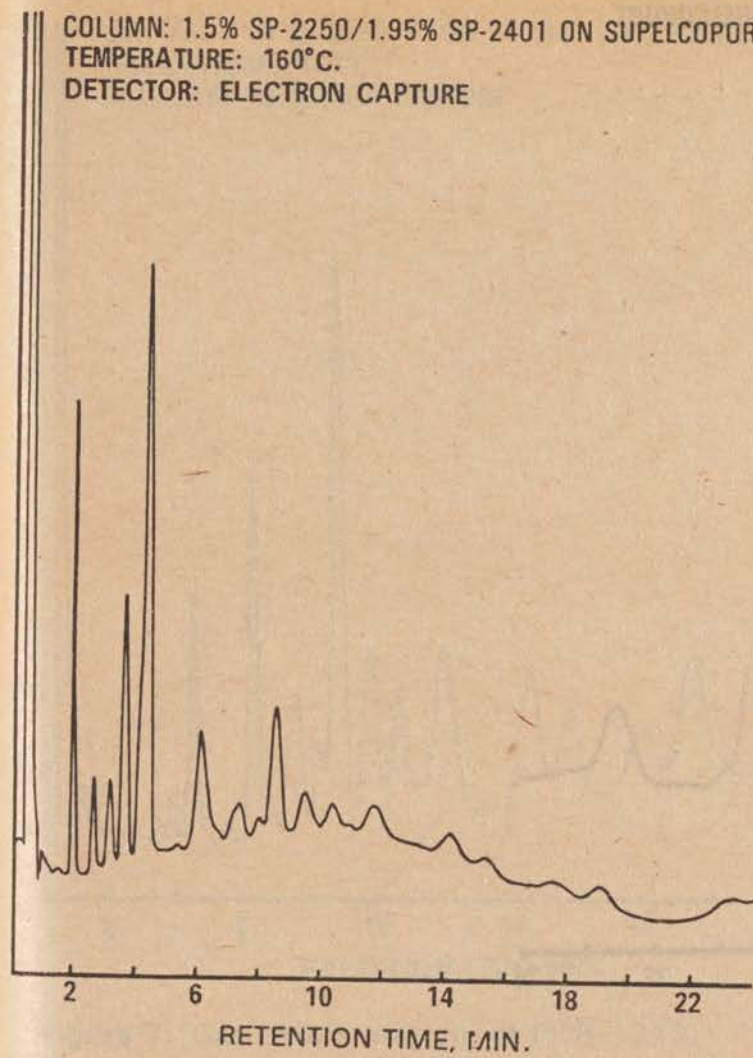


Figure 5. Gas chromatogram of PCB-1221.

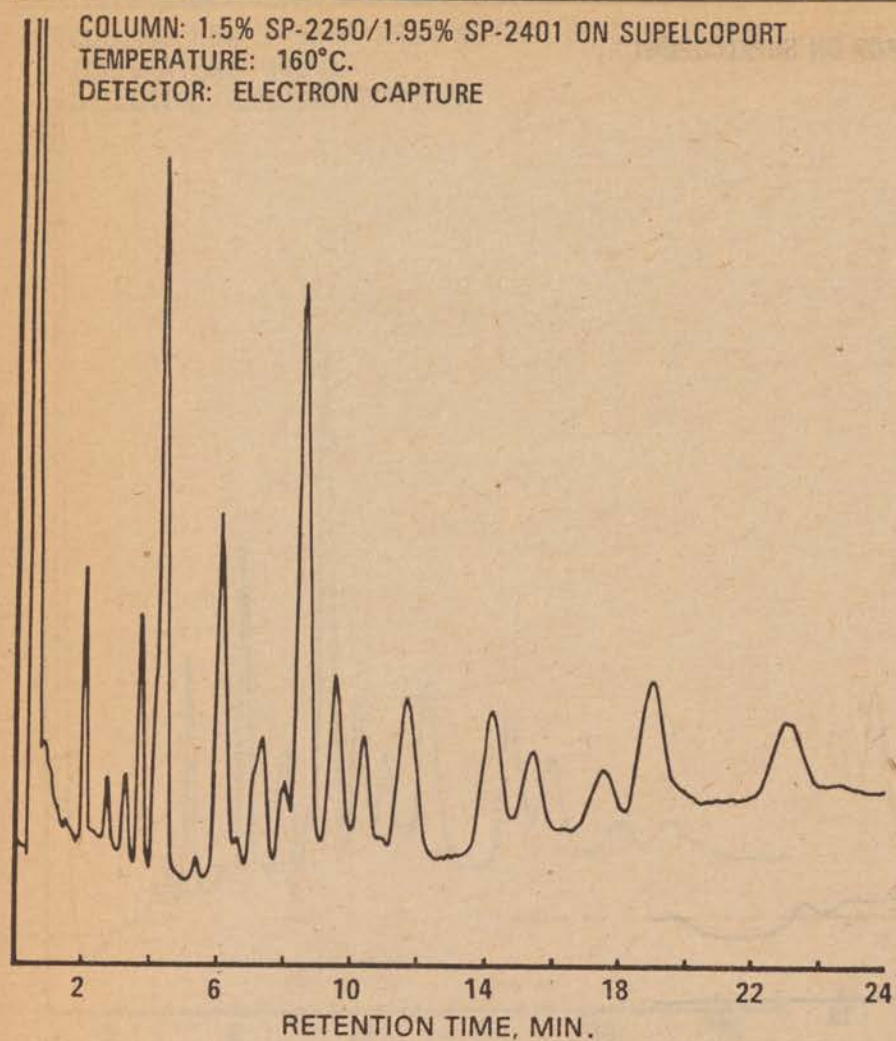


Figure 6. Gas chromatogram of PCB-1232.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

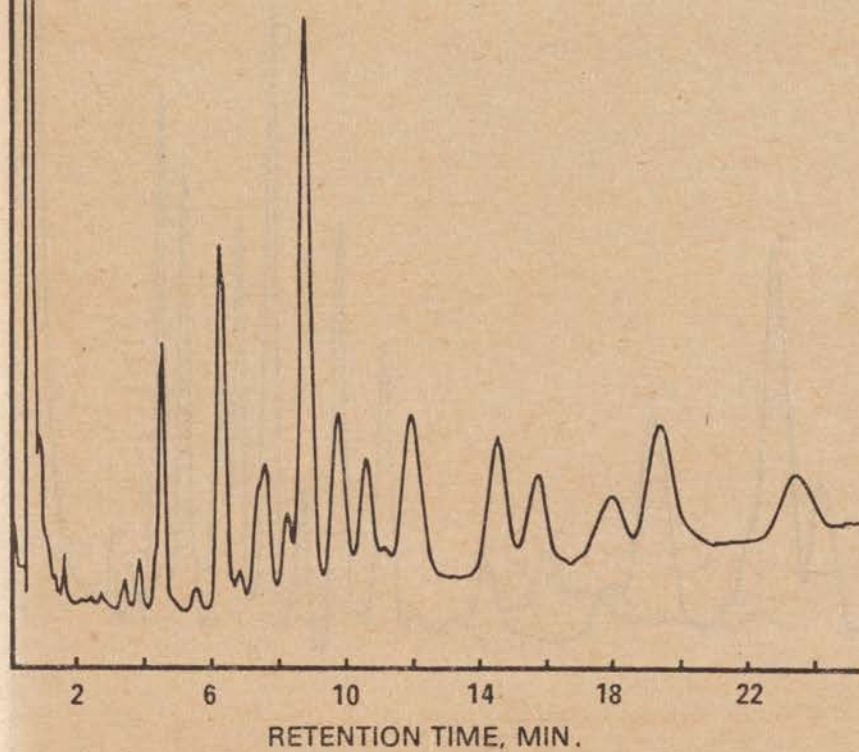


Figure 7. Gas chromatogram of PCB-1242.

COLUMN: 1.5% SP-2250/1.95% SP-2401 ON SUPELCOPORT
TEMPERATURE: 160°C.
DETECTOR: ELECTRON CAPTURE

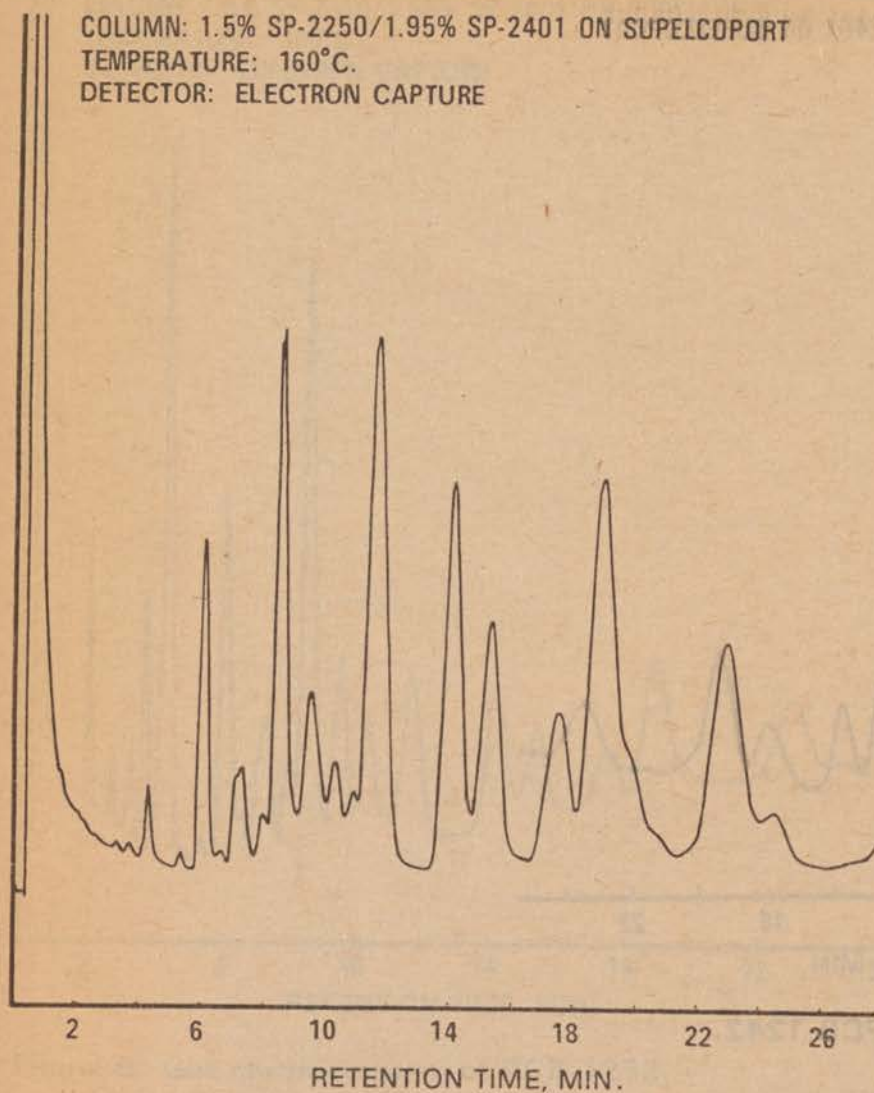


Figure 8. Gas chromatogram of PCB-1248.

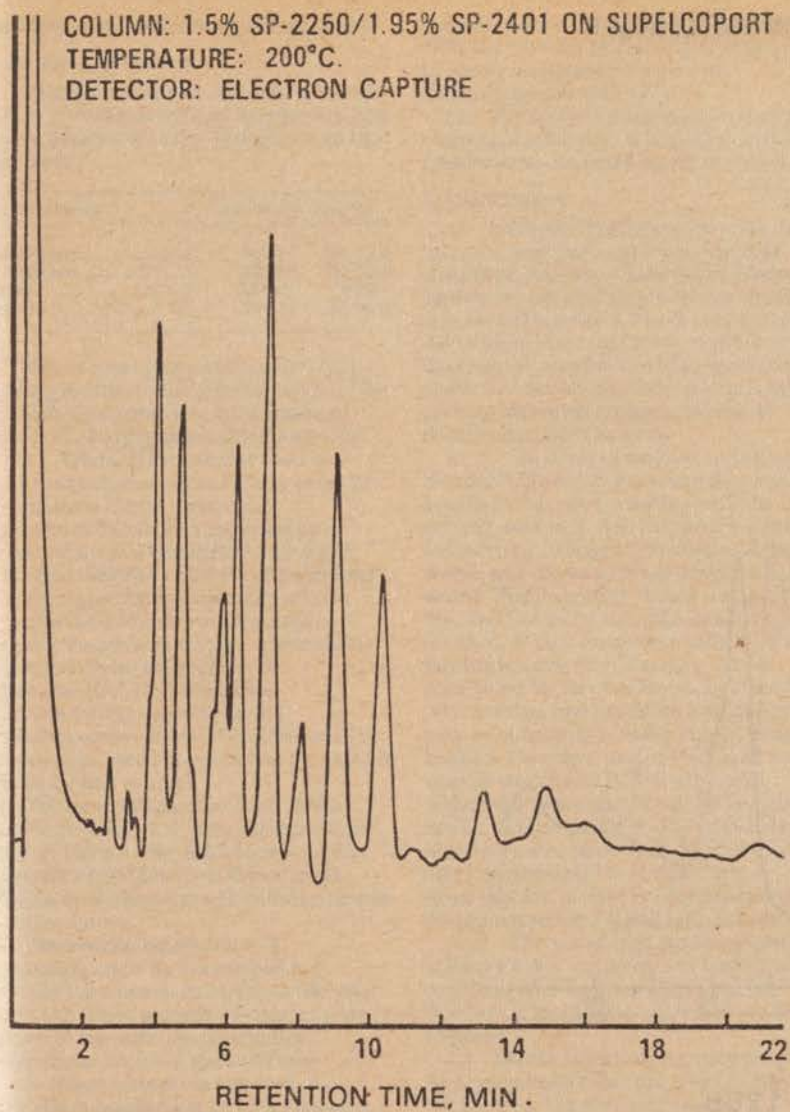


Figure 9. Gas chromatogram of PCB-1254.

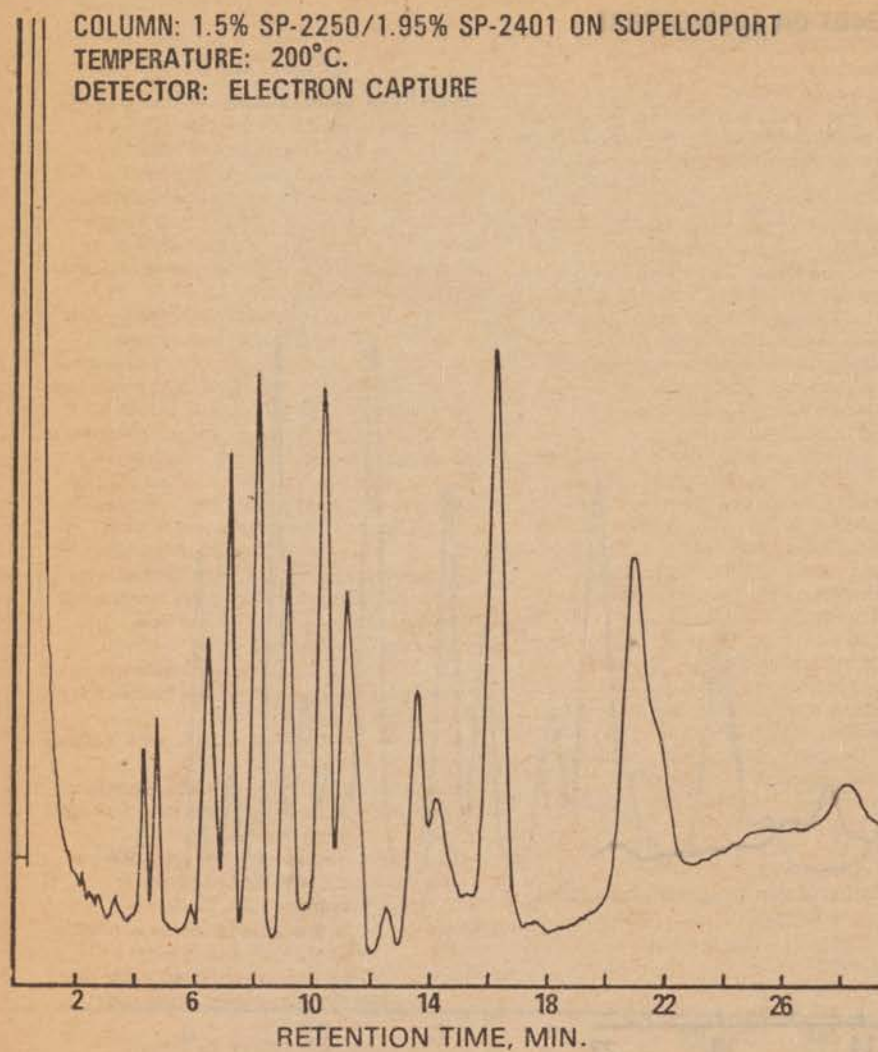


Figure 10. Gas chromatogram of PCB-1260.

Method 609—Nitroaromatics and Isophorone**1. Scope and Application**

1.1 This method covers the determination of certain nitroaromatics and isophorone. The following parameters may be determined by this method:

Parameter	Storet No.	Gas No.
2,4-Dinitrotoluene.....	34611	121-14-2
2,6-Dinitrotoluene.....	34626	606-20-2
Isophorone.....	34408	78-59-1
Nitrobenzene.....	34447	98-95-3

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 608, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. Isophorone and nitrobenzene are measured by flame

ionization detector gas chromatography (FIDGC). The dinitrotoluenes are measured by electron capture detector gas chromatography (ECDGC).²

2.2 The method provides a Florisil column cleanup procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified⁴⁻⁶ for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long x 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—100 mm long x 10 mm ID, with Teflon stopcock.

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.8 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.2 m long x 2 or 4 mm ID glass, packed with 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or equivalent. This column was used to develop the method performance statements given in Section 14.

Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—3.0 m long x 2 or 4 mm ID glass, packed with 3% OV-101 on Gas-Chrom Q (80/100 mesh) or equivalent.

5.6.3 Detectors—Flame ionization and electron capture detectors. The flame ionization detector (FID) is used when determining isophorone and nitrobenzene. The electron capture detector (ECD) is used when determining the dinitrotoluenes. Both detectors have proven effective in the analysis of wastewaters and were used in develop the method performance statements in Section 14. Guidelines for the use to alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sulfuric acid (1+1)—Slowly, add 50 mL of H₂SO₄ (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.4 Acetone, hexane, methanol, methylene chloride—Pesticide quality or equivalent.

6.5 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.6 Florisil—PR grade (60/100 mesh). Purchase activated at 1250 °F and store in dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 200 °C in a foil-covered glass container and allow to cool.

6.7 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic

system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (< 10% relative standard deviation, RSD) linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (< 10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is}, vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ± 15%, a new calibration curve must be prepared for that compound.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest in acetone at a concentration of 20 µg/mL for each dinitrotoluene and 100 µg/mL for isophorone and nitrobenzene. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 2 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) Calculate accuracy ($\bar{X}$) using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S) using the equation in Table 3, substituting $\bar{X}$ for $\bar{X}S$; (3) calculate the range for recovery at the spike concentration as $100 \bar{X}/T \pm 2.44 (100 S/T)\%$.⁷

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these

criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P-2s_p$ to $P+2s_p$. If $PO=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling.

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁸ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5 to 9 with sodium hydroxide solution or sulfuric acid.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the

emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Sections 10.7 and 10.8 describe a procedure for exchanging the methylene chloride solvent to hexane while concentrating the extract volume to 1.0 mL. When it is not necessary to achieve the MDL in Table 2, the solvent exchange may be made by the addition of 50 mL of hexane and concentration to 10 mL as described in Method 606, Sections 10.7 and 10.8.

10.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Add 1 to 2 mL of hexane and a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top. Place the micro-K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL,

remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.9 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of hexane. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use the procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure.

11.2 Florisil column cleanup:

11.2.1 Prepare a slurry of 10 g of activated Florisil in methylene chloride/hexane (1+9)(V/V) and place the Florisil into a chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

11.2.2 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1+9)(V/V) and continue the elution of the column. Discard the eluate.

11.2.3 Next, elute the column with 30 mL of acetone/methylene chloride (1+9)(V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction as in Sections 10.6, 10.7, 10.8, and 10.9 including the solvent exchange to 1 mL of hexane. This fraction should contain the nitroaromatics and isophorone. Analyze by gas chromatography (Section 12).

12. Gas Chromatography

12.1 Isophorone and nitrobenzene are analyzed by injection of a portion of the extract into an FIDGC. The dinitrotoluenes are analyzed by a separate injection into an ECDGC. Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 1 are shown in Figures 1 and 2. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the same extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 μ L of the sample extract or standard into the gas chromatograph using the solvent-flush technique.⁹ Smaller (1.0 μ L) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_e)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (μ L).

V_e = Volume of total extract (μ L).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.
 I_s = Amount of internal standard added to each extract (μg).
 V_o = Volume of water extracted (L).

13.2 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹⁰ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from $7 \times \text{MDL}$ to $1000 \times \text{MDL}$.¹⁰

14.3 This method was tested by 18 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 515 $\mu\text{g/L}$.¹¹ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

- 40 CFR Part 136, Appendix B.
- "Determination of Nitroaromatics and Isophorone in Industrial and Municipal Wastewaters," EPA-600/4-82-024, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1982.
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Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

5. "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

6. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

7. Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

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9. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).

10. "Determination of Method Detection Limit and Analytical Curve for EPA Method 609—Nitroaromatics and Isophorone," Special letter report for EPA Contract 68-03-2624, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

11. "EPA Method Validation Study 19, Method 609 (Nitroaromatics and Isophorone)," Report for EPA Contract 68-03-2624 (In preparation).

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit ($\mu\text{g/L}$)	
	Col. 1	Col. 2	ECDGC	FIDGC
Nitrobenzene	3.31	4.31	13.7	3.6
2,6-Dinitrotoluene	3.52	4.75	0.01	—
Isophorone	4.49	5.72	15.7	5.7
2,4-Dinitrotoluene	5.35	6.54	0.02	—

Column 1 conditions: Gas-Chrom Q (80/100 mesh) coated with 1.95% QF-1/1.5% OV-17 packed in a 1.2 m long $\times$ 2 mm or 4 mm ID glass column. A 2 mm ID column and nitrogen carrier gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by FIDGC. The

column temperature was held isothermal at 85 °C. A 4 mm ID column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used when determining the dinitrotoluenes by ECDGC. The column temperature was held isothermal at 145 °C.

Column 2 conditions: Gas-Chrom Q (80/100 mesh) coated with 3% OV-101 packed in a 3.0 m long $\times$ 2 mm or 4 mm ID glass column. A 2 mm ID column and nitrogen carrier gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by FIDGC. The column temperature was held isothermal at 100 °C. A 4 mm ID column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used when determining the dinitrotoluenes by ECDGC. The column temperature was held isothermal at 150 °C.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 609

Parameter	Test Conc. ($\mu\text{g/L}$)	Limit for s ($\mu\text{g/L}$)	Range for $\bar{X}$ ($\mu\text{g/L}$)	Range for P, P _r (%)
2,4-Dinitrotoluene	20	5.1	3.6-22.8	6-125
2,6-Dinitrotoluene	20	4.8	3.8-23.0	8-126
Isophorone	100	32.3	8.0-100.0	D-117
Nitrobenzene	100	33.3	25.7-100.0	6-118

s = Standard deviation of four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

P, P_r = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 609

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single analyst precision, s_r ($\mu\text{g/L}$)	Overall precision, S_r ($\mu\text{g/L}$)
2,4-Dinitrotoluene	$0.65C + 0.22$	$0.20\bar{X} + 0.08$	$0.37\bar{X} - 0.07$
2,6-Dinitrotoluene	$0.66C + 0.20$	$0.19\bar{X} + 0.06$	$0.36\bar{X} - 0.00$
Isophorone	$0.49C + 2.93$	$0.28\bar{X} + 2.77$	$0.46\bar{X} + 0.31$
Nitrobenzene	$0.60C + 2.00$	$0.25\bar{X} + 2.53$	$0.37\bar{X} - 0.78$

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_r = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S_r = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

BILLING CODE 6560-50-M

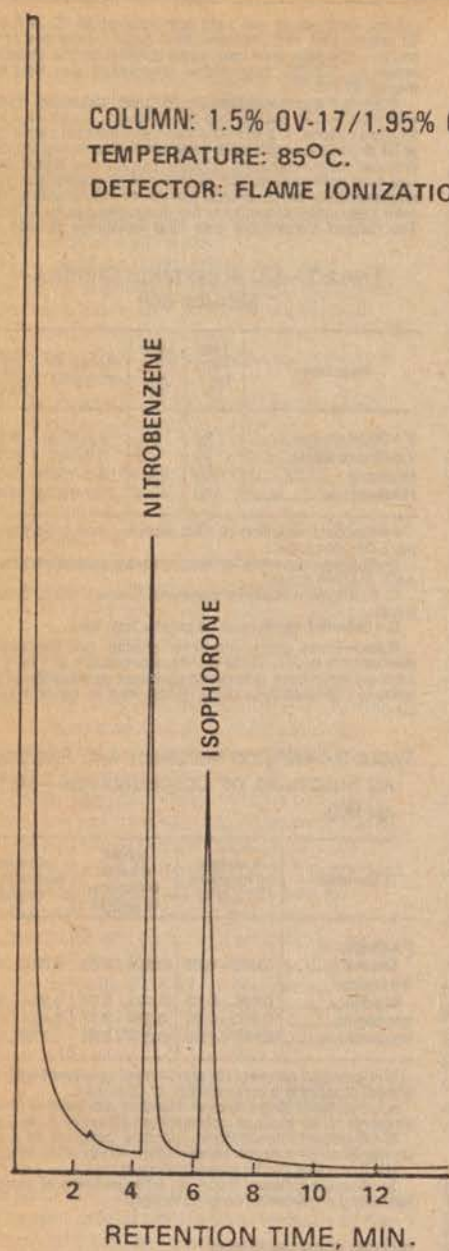


Figure 1. Gas chromatogram of nitrobenzene and isophorone.

COLUMN: 1.5% OV-17/1.95% QF-1 ON GAS CHROM Q

TEMPERATURE: 145°C.

DETECTOR: ELECTRON CAPTURE

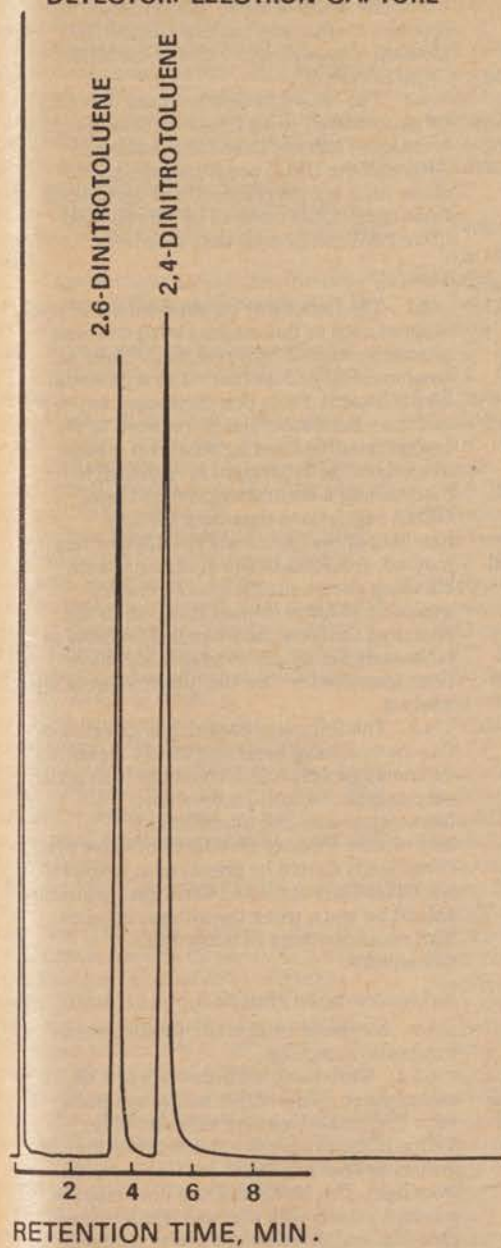


Figure 2. Gas chromatogram of dinitrotoluenes.

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Method 610—Polynuclear Aromatic Hydrocarbons

1. Scope and Application

1.1 This method covers the determination of certain polynuclear aromatic hydrocarbons (PAH). The following parameters can be determined by this method:

Parameter	Storet No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Benzo(a)anthracene	34526	56-55-3
Benzo(a)pyrene	34247	50-32-8
Benzo(b)fluoranthene	34230	205-99-2
Benzo(g,h,i)perylene	34521	191-24-2
Benzo(k)fluoranthene	34242	207-08-9
Chrysene	34320	218-01-8
Dibenzo(a,h)anthracene	34556	53-70-3
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Indeno(1,2,3-cd)pyrene	34403	193-39-5
Naphthalene	34696	91-20-3
Phenanthrene	34461	85-01-6
Pyrene	34469	129-00-0

1.2 This is a chromatographic method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for many of the parameters listed above, using the extract produced by this method.

1.3 This method provides for both high performance liquid chromatographic (HPLC) and gas chromatographic (GC) approaches for the determination of PAHs. The gas chromatographic procedure does not adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. Unless the purpose for the analysis can be served by reporting the sum of an unresolved pair, the liquid chromatographic approach must be used for these compounds. The liquid chromatographic method does resolve all 16 of the PAHs listed.

1.4 The method detection limit (MDL, defined in Section 15.1) ¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 608, 609, 611, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. Selection of the aliquots must be made prior to the solvent exchange steps of this method. The analyst is allowed the latitude, under

Sections 12 and 13, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.6 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.7 This method is restricted to use by or under the supervision of analysts experienced in the use of HPLC and GC systems and in the interpretation of liquid and gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and concentrated to a volume of 10 mL or less. The extract is then separated by HPLC or GC. Ultraviolet (UV) and fluorescence detectors are used with HPLC to identify and measure the PAHs. A flame ionization detector is used with GC.²

2.2 The method provides a silica gel column cleanup procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference.

Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature

and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in table 1.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ⁴⁻⁶ for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzo(a)pyrene, and dibenzo(a,h)anthracene. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long $\times$ 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Chromatographic column—250 mm long $\times$ 10 mm ID, with coarse frit filter disc at bottom and Teflon stopcock.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 High performance liquid chromatograph (HPLC)—An analytical system complete with column supplies, high pressure syringes, detectors, and compatible strip-chart recorder. A data system is recommended for measuring peak areas and retention times.

5.6.1 Gradient pumping system—Constant flow.

5.6.2 Reverse phase column—HC-ODS Sil-X, 5 micron particle diameter, in a 25 cm $\times$ 2.6 mm ID stainless steel column (Perkin Elmer No. 089-0716 or equivalent). This column was used to develop the method performance statements in Section 15. Guidelines for the use of alternate column packings are provided in Section 12.2.

5.6.3 Detectors—Fluorescence and/or UV detectors. The fluorescence detector is used for excitation at 280 nm and emission greater than 389 nm cutoff (Corning 3-75 or equivalent). Fluorometers should have dispersive optics for excitation and can utilize either filter or dispersive optics at the emission detector. The UV detector is used at 254 nm and should be coupled to the fluorescence detector. These detectors were used to develop the method performance statements in Section 15. Guidelines for the use of alternate detectors are provided in Section 12.2.

5.7 Gas chromatograph—An analytical system complete with temperature programmable gas chromatograph suitable for on-column or splitless injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.7.1 Column—1.8 m long $\times$ 2 mm ID glass, packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

This column was used to develop the retention time data in Table 2. Guidelines for the use of alternate column packings are provided in Section 13.3.

5.7.2 Detector—Flame ionization detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), excluding the four pairs of unresolved compounds listed in Section 1.3. Guidelines for the use of alternate detectors are provided in Section 13.3.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Cyclohexane, methanol, acetone, methylene chloride, pentane—Pesticide quality or equivalent.

6.4 Acetonitrile—HPLC quality, distilled in glass.

6.5 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.6 Silica gel—100/200 mesh, desiccant, Davison, grade-923 or equivalent. Before use, activate for at least 16 h at 130 °C in a shallow glass tray, loosely covered with foil.

6.7 Stock standard solutions (1.00 μ g/ μ L)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in acetonitrile and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish liquid or gas chromatographic operating conditions equivalent to those given in Table 1 or 2. The chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a

volumetric flask and diluting to volume with acetonitrile. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 5 to 25 μ L for HPLC and 2 to 5 μ L for GC, analyze each calibration standard according to Section 12 or 13, as appropriate. Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range ($<10\%$ relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with acetonitrile. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 5 to 25 μ L for HPLC and 2 to 5 μ L for GC, analyze each calibration standard according to Section 12 or 13, as appropriate. Tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (μ g/L).

C_s = Concentration of the parameter to be measured (μ g/L).

If the RF value over the working range is a constant ($<10\%$ RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, 12.2, and 13.3) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the

analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at the following concentrations in acetonitrile: 100 $\mu\text{g/mL}$ of any of the six early-eluting PAHs (naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene); 5 $\mu\text{g/mL}$ of benzo(k)fluoranthene; and 10 $\mu\text{g/mL}$ of any of the other PAHs. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 3 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in $\mu\text{g/L}$, and the standard deviation of the recovery (s) in $\mu\text{g/L}$, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 3. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 3 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none, (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 3. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 3, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 4, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 4, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X' / T) \pm 2.44(100 S' / T)\%$.⁷

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the

laboratory. If the entire list of parameters in Table 3 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_r) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_r) for each parameter with the corresponding QC acceptance criteria found in Table 3. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁸ should be followed, except that the bottle must not be pre-rinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. PAHs are known to be light sensitive; therefore, samples, extracts, and standards should be stored in amber or foil-wrapped bottles in order to minimize photolytic decomposition. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁹ Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min. with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL,

remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.7 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial and protected from light. If the sample extract requires no further cleanup, proceed with gas or liquid chromatographic analysis (Section 12 or 13). If the sample requires further cleanup, proceed to Section 11.

10.8 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use the procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the methods as revised to incorporate the cleanup procedure.

11.2 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add 1 to 10 mL of the sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100 °C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the extract volume to about 2 mL.

11.3 Silica gel column cleanup for PAHs:

11.3.1 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10-mm ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

11.3.2 Prewet the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2-mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium

sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

11.3.3 Next, elute the column with 25 mL of methylene chloride/pentane (4+6)(V/V) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to less than 10 mL as in Section 10.6. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint with pentane. Proceed with HPLC or GC analysis.

12. High Performance Liquid Chromatography

12.1 To the extract in the concentrator tube, add 4 mL of acetonitrile and a new boiling chip, then attach a two-ball micro-Snyder column. Concentrate the solvent as in Section 10.6, except set the water bath at 95 to 100 °C. When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of acetonitrile. Adjust the extract volume to 1.0 mL.

12.2 Table 1 summarizes the recommended operating conditions for the HPLC. Included in this table are retention times, capacity factors, and MDL that can be achieved under these conditions. The UV detector is recommended for the determination of naphthalene, acenaphthylene, acenaphthene, and fluorene and the fluorescence detector is recommended for the remaining PAHs. Examples of the separations achieved by this HPLC column are shown in Figures 1 and 2. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.3 Calibrate the system daily as described in Section 7.

12.4 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the instrument.

12.5 Inject 5 to 25 µL of the sample extract or standard into the HPLC using a high pressure syringe or a constant volume sample injection loop. Record the volume injected to the nearest 0.1 µL, and the resulting peak size in area or peak height units. Re-equilibrate the HPLC column at the initial gradient conditions for at least 10 min between injections.

12.6 Identify the parameters in the sample by comparing the retention time of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.7 If the response for a peak exceeds the working range of the system, dilute the extract with acetonitrile and reanalyze.

12.8 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Gas Chromatography

13.1 The packed column GC procedure will not resolve certain isomeric pairs as indicated in Section 1.3 and Table 2. The liquid chromatographic procedure (Section 12) must be used for these parameters.

13.2 To achieve maximum sensitivity with this method, the extract must be concentrated to 1.0 mL. Add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of methylene chloride. Adjust the final volume to 1.0 mL and stopper the concentrator tube.

13.3 Table 2 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times that were obtained under these conditions. An example of the separations achieved by this column is shown in Figure 3. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

13.4 Calibrate the gas chromatographic system daily as described in Section 7.

13.5 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

13.6 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.¹⁰ Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, and the resulting peak size in area or peak height units.

13.7 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

13.8 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

13.9 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

14. Calculations

14.1 Determine the concentration of individual compounds in the sample.

14.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(V_i)}{(V_i)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_t = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

14.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2. and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_s = Volume of water extracted (L).

14.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

15. Method Performance

15.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹¹ Similar results were achieved using representative wastewaters. MDL for the GC approach were not determined. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

15.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 × MDL to 800 × MDL¹¹ with the following exception: benzo(ghi)perylene recovery at 80 × and 800 × MDL were low (35% and 45%, respectively).

15.3 This method was tested by 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations

over the range 0.1 to 425 $\mu\text{g/L}$.¹² Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

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TABLE 1.—HIGH PERFORMANCE LIQUID CHROMATOGRAPHY CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Column capacity factor (k')	Method detection limit ($\mu\text{g/L}$) ^a
Naphthalene	16.6	12.2	1.8
Acenaphthylene	18.5	13.7	2.3
Acenaphthene	20.5	15.2	1.8
Fluorene	21.2	15.8	0.21
Phenanthrene	22.1	16.6	0.64
Anthracene	23.4	17.6	0.66
Fluoranthene	24.5	18.5	0.21
Pyrene	25.4	19.1	0.27
Benzo(a)anthracene	28.5	21.6	0.013
Chrysene	29.3	22.2	0.15
Benzo(b)fluoranthene	31.6	24.0	0.018
Benzo(k)fluoranthene	32.9	25.1	0.017
Benzo(a)pyrene	33.9	25.9	0.023
Dibenzo(a,h)anthracene	35.7	27.4	0.030
Benzo(ghi)perylene	36.3	27.8	0.076
Indeno(1,2,3-cd)pyrene	37.4	28.7	0.043

HPLC column conditions: Reverse phase HC-ODS SII-X, 5 micron particle size, in a 25 cm $\times$ 2.6 mm ID stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4+6), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

^aThe MDL for naphthalene, acenaphthylene, acenaphthene, and fluorene were determined using a UV detector. All others were determined using a fluorescence detector.

TABLE 2.—GAS CHROMATOGRAPHIC CONDITIONS AND RETENTION TIMES

Parameter	Retention time (min)
Naphthalene	4.5
Acenaphthylene	10.4
Acenaphthene	10.8
Fluorene	12.6
Phenanthrene	15.9
Anthracene	15.9
Fluoranthene	19.8
Pyrene	20.6
Benzo(a)anthracene	24.7
Chrysene	24.7
Benzo(b)fluoranthene	28.0
Benzo(k)fluoranthene	28.0
Benzo(a)pyrene	29.4
Dibenzo(a,h)anthracene	36.2
Indeno(1,2,3-cd)pyrene	36.2
Benzo(ghi)perylene	38.6

GC Column conditions: Chromosorb W-AW-DCMS (100/120 mesh) coated with 3% OV-17 packed in a 1.8 $\times$ 2 mm ID glass column with nitrogen carrier gas at 40 mL/min flow rate. Column temperature was held at 100 °C for 4 min, then programmed at 8 °C/min to a final hold at 280 °C.

TABLE 3.—QC ACCEPTANCE CRITERIA—METHOD 610

Parameter	Test conc. ($\mu\text{g/L}$)	Limit for s ($\mu\text{g/L}$)	Range for $\bar{X}$ ($\mu\text{g/L}$)	Range for P, P _s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

NOTE.—These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 610

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single analyst precision, s _r ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Acenaphthene	0.52C + 0.54	0.39 $\bar{X}$ + 0.76	0.53 $\bar{X}$ + 1.32
Acenaphthylene	0.69C - 1.89	0.36 $\bar{X}$ + 0.29	0.42 $\bar{X}$ + 0.52
Anthracene	0.63C - 1.26	0.23 $\bar{X}$ + 1.16	0.41 $\bar{X}$ + 0.45
Benzo(a)anthracene	0.73C + 0.05	0.28 $\bar{X}$ + 0.04	0.34 $\bar{X}$ + 0.02
Benzo(a)pyrene	0.56C + 0.01	0.38 $\bar{X}$ - 0.01	0.53 $\bar{X}$ - 0.01
Benzo(b)fluoranthene	0.78C + 0.01	0.21 $\bar{X}$ + 0.01	0.38 $\bar{X}$ - 0.00
Benzo(ghi)perylene	0.44C + 0.30	0.25 $\bar{X}$ + 0.04	0.58 $\bar{X}$ + 0.10
Benzo(k)fluoranthene	0.59C + 0.00	0.44 $\bar{X}$ - 0.00	0.69 $\bar{X}$ + 0.01
Chrysene	0.77C - 0.18	0.32 $\bar{X}$ - 0.18	0.66 $\bar{X}$ - 0.22
Dibenzo(a,h)anthracene	0.41C + 0.11	0.24 $\bar{X}$ + 0.02	0.45 $\bar{X}$ + 0.03
Fluoranthene	0.68C + 0.07	0.22 $\bar{X}$ + 0.06	0.32 $\bar{X}$ + 0.03
Fluorene	0.56C - 0.52	0.44 $\bar{X}$ - 1.12	0.63 $\bar{X}$ - 0.65
Indeno(1,2,3-cd)pyrene	0.54C + 0.06	0.29 $\bar{X}$ + 0.02	0.42 $\bar{X}$ + 0.01
Naphthalene	0.57C - 0.70	0.39 $\bar{X}$ - 0.18	0.41 $\bar{X}$ - 0.74
Phenanthrene	0.72C - 0.95	0.29 $\bar{X}$ + 0.05	0.47 $\bar{X}$ - 0.25
Pyrene	0.69C - 0.12	0.25 $\bar{X}$ + 0.14	0.42 $\bar{X}$ - 0.00

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_r = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

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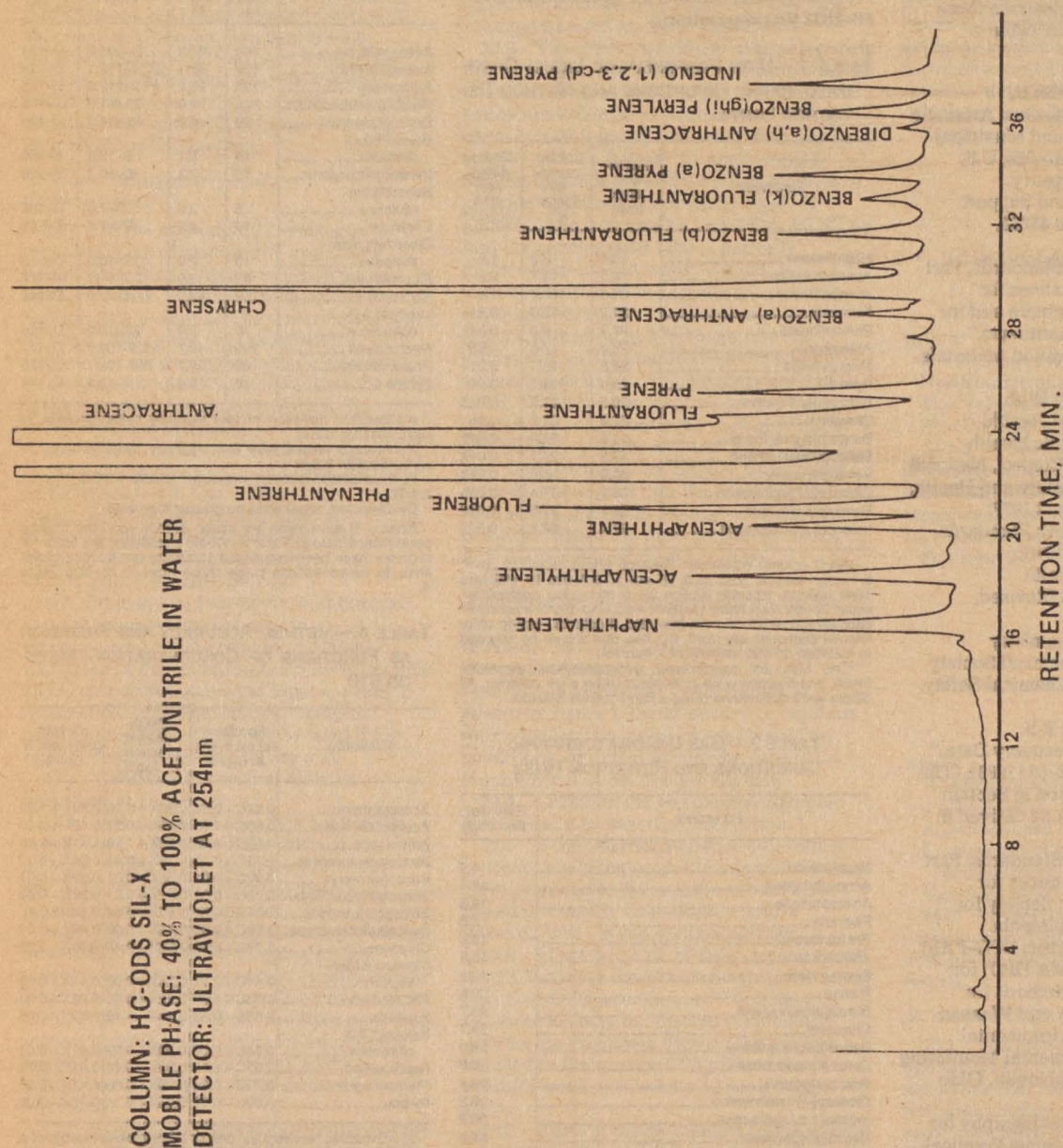


Figure 1. Liquid chromatogram of polynuclear aromatic hydrocarbons.

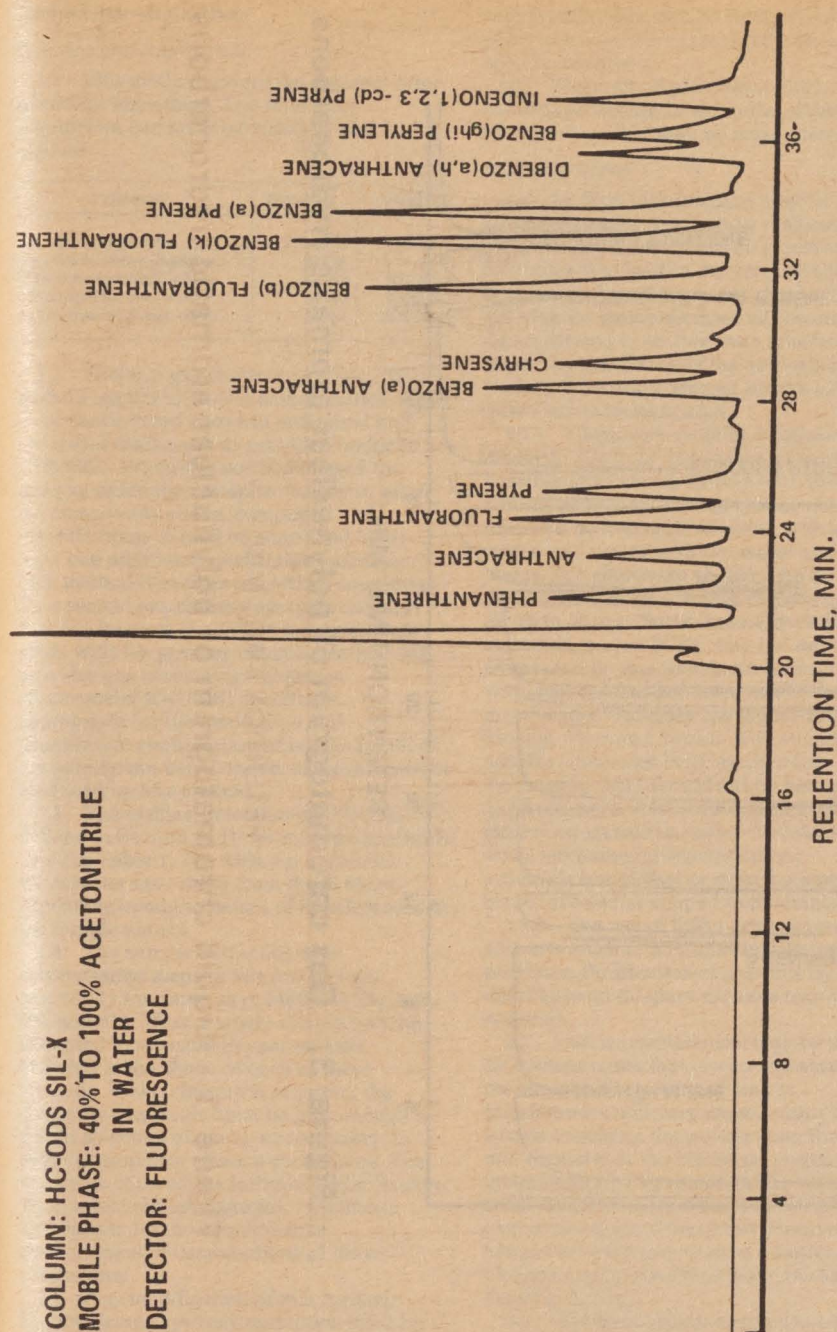


Figure 2. Liquid chromatogram of polynuclear aromatic hydrocarbons.

COLUMN: 3% OV-17 ON CHROMOSORB W-AW-DCMS
PROGRAM: 100°C FOR 4 MIN, 8°C/MIN TO 280°C
DETECTOR: FLAME IONIZATION

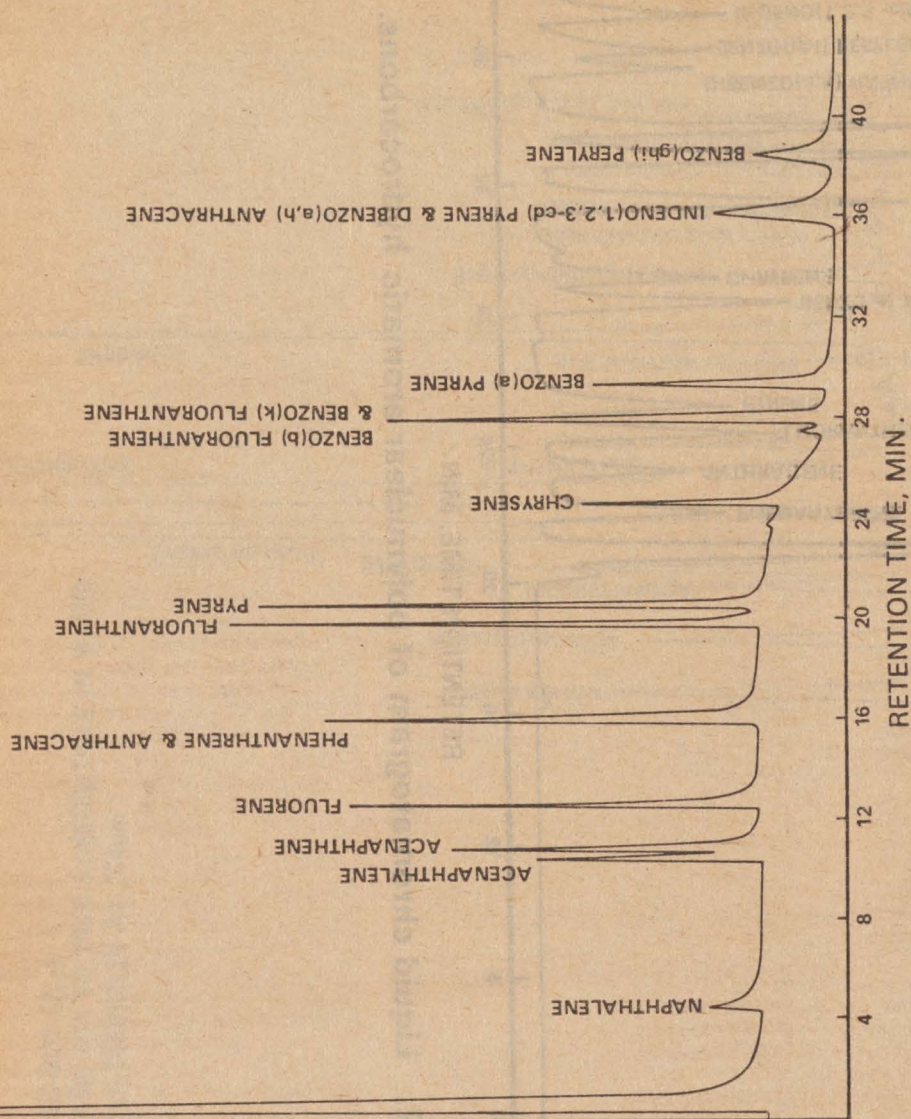


Figure 3. Gas chromatogram of polynuclear aromatic hydrocarbons.

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Method 611—Haloethers**1. Scope and Application**

1.1 This method covers the determination of certain haloethers. The following parameters can be determined by this method:

Parameter	Storet No.	CAS No.
Bis(2-chloroethyl) ether.....	34273	111-44-4
Bis(2-chloroethoxy) methane.....	34278	111-91-1
Bis(2-chloroisopropyl) ether.....	34283	108-60-1
4-Bromophenyl phenyl ether.....	34636	101-55-3
4-Chlorophenyl phenyl ether.....	34641	7005-72-3

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 608, 609, and 612. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is

separated by gas chromatography and the parameters are then measured with a halide specific detector.²

2.2 The method provides a Florisil column cleanup procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference.

Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present together in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this

method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified⁴⁻⁶ for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long x 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—400 mm long x 19 mm ID, with Teflon stopcock and coarse frit filter disc at bottom (Kontes K-420540-0224 or equivalent).

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical

columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long x 2 mm ID glass, packed with 3% SP-1000 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long x 2 mm ID glass, packed with 2,6-diphenylene oxide polymer (60/80 mesh), Tenax, or equivalent.

5.6.3 Detector—Halide specific detector: electrolytic conductivity or microcoulometric. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1). The Hall conductivity detector was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1. Although less selective, an electron capture detector is an acceptable alternative.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Acetone, hexane, methanol, methylene chloride, petroleum ether (boiling range 30–60 °C)—Pesticide quality or equivalent.

6.4 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.5 Florisil—PR Grade (60/100 mesh). Purchase activated at 1250 °F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130 °C in a foil-covered glass container and allow to cool.

6.6 Ethyl ether—Nanograde, redistilled in glass if necessary.

6.6.1 Ethyl ether must be shown to be free of peroxides before it is used as indicated by EM Laboratories Quant test strips. (Available from Scientific Products Co., Cat. No. P1126-8, and other suppliers.)

6.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

6.7 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in acetone and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light.

Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.8 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 µL, analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard (µg/L).

C_s = Concentration of the parameter to be measured (µg/L).

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±15%, a new calibration curve must be prepared for that compound.

7.5 The cleanup procedure in Section 11 utilizes Florisil column chromatography. Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value⁷ is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g.

7.6 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of

measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 µg/mL in acetone. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter. Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.* If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X' / T) \pm 2.44(100 S' / T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

NOTE.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P}-2s_p$ to $\bar{P}+2s_p$. If $\bar{P}=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁹ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.¹⁰ Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

Note.—Some of the haloethers are very volatile and significant losses will occur in

concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D apparatus from the hot water bath.

10.7 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Raise the temperature of the water bath to 85 to 90 °C. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use the procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure.

11.2 Florisil column cleanup for haloethers:

11.2.1 Adjust the sample extract volume to 10 mL.

11.2.2 Place a weight of Florisil (nominally 20 g) predetermined by calibration (Section 7.5), into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.3 Preelute the column with 50 to 60 mL of petroleum ether. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 300 mL of ethyl ether/petroleum ether (6+94) (V/V). Adjust the elution rate to approximately 5 mL/min and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the haloethers.

11.2.4 Concentrate the fraction as in Section 10.6, except use hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the volume of the cleaned up extract to 10 mL with hexane and analyze by gas chromatography (Section 12).

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Columns 1 and 2 are shown in Figures 1 and 2, respectively. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.¹¹ Smaller (1.0 µL) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weight heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration, } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_j)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_j = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.A_{is} = Response for the internal standard.I_s = Amount of internal standard added to each extract (μg).V_o = Volume of water extracted (L).

13.2 Report results in μg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water.¹² Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4 × MDL to 1000 × MDL.¹²

14.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 626 μg/L.¹² Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

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11. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis: Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHODS DETECTION LIMITS

Parameters	Retention time (min)		Method detection limit (μg/L)
	Column 1	Column 2	
Bis (2-chloroisopropyl) ether.....	9.4	9.7	0.8
Bis (2-chloroethyl) ether.....	9.3	9.1	0.3
Bis (2-chloroethoxy) methane.....	13.1	10.0	0.5
4-Chlorophenyl ether.....	19.4	15.0	3.9
4-Bromophenyl phenyl ether.....	21.2	16.2	2.3

Column 1 conditions: Supelcoport (100/120 mesh) coated with 3% SP-1000 packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 60 °C for 2 min after injection then programmed at 8 °C/min to 230 °C and held for 4 min. Under these conditions the retention time for Aldrin is 22.6 min.

Column 2 conditions: Tenax-GC (60/80 mesh) packed in a 1.8 m long x 2 mm ID glass column with helium carrier gas at 40 mL/min flow rate. Column temperature held at 150 °C for 4 min after injection then programmed at 16 °C/min to

310 °C. Under these conditions the retention time for Aldrin is 18.4 min.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 611

Parameter	Test conc. (μg/L)	Limit for s (μg/L)	Range for $\bar{X}$ (μg/L)	Range for P, P _s percent
Bis(2-chloroethyl) ether.....	100	26.3	26.3-136.8	11-152
Bis(2-chloroethoxy) methane.....	100	25.7	27.3-115.0	12-128
Bis(2-chloroisopropyl) ether.....	100	32.7	26.4-147.0	9-165
4-Bromophenyl phenyl ether.....	100	39.3	7.5-167.5	D-189
4-Chlorophenyl phenyl ether.....	100	30.7	15.4-152.5	D-170

s = Standard deviation of four recovery measurements, in μg/L (Section 8.2.4).

$\bar{X}$ = Average recovery for four recovery measurements, in μg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 611

Parameter	Accuracy, as recovery, X' (μg/L)	Single analyst precision, s _s (μg/L)	Overall precision, S' (μg/L)
Bis(2-chloroethyl) ether.....	0.81C + 0.54	0.19 $\bar{X}$ + 0.28	0.35 $\bar{X}$ + 0.36
Bis(2-chloroethoxy) methane.....	0.71C + 0.13	0.20 $\bar{X}$ + 0.15	0.33 $\bar{X}$ + 0.11
Bis(2-chloroisopropyl) ether.....	0.85C + 1.67	0.20 $\bar{X}$ + 1.05	0.36 $\bar{X}$ + 0.79
4-Bromophenyl phenyl ether.....	0.84C + 2.55	0.25 $\bar{X}$ + 0.21	0.47 $\bar{X}$ + 0.37
4-Chlorophenyl phenyl ether.....	0.82C + 1.97	0.18 $\bar{X}$ + 2.13	0.41 $\bar{X}$ + 0.55

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in μg/L.

s_s = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in μg/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in μg/L.

C = True value for the concentration, in μg/L.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in μg/L.

BILLING CODE 6550-50-M.

COLUMN: 3% SP-1000 ON SUPELCOPORT
PROGRAM 60°C FOR 2 MIN, 8°C/MIN TO 230°C
DETECTOR: HALL ELECTROLYTIC CONDUCTIVITY

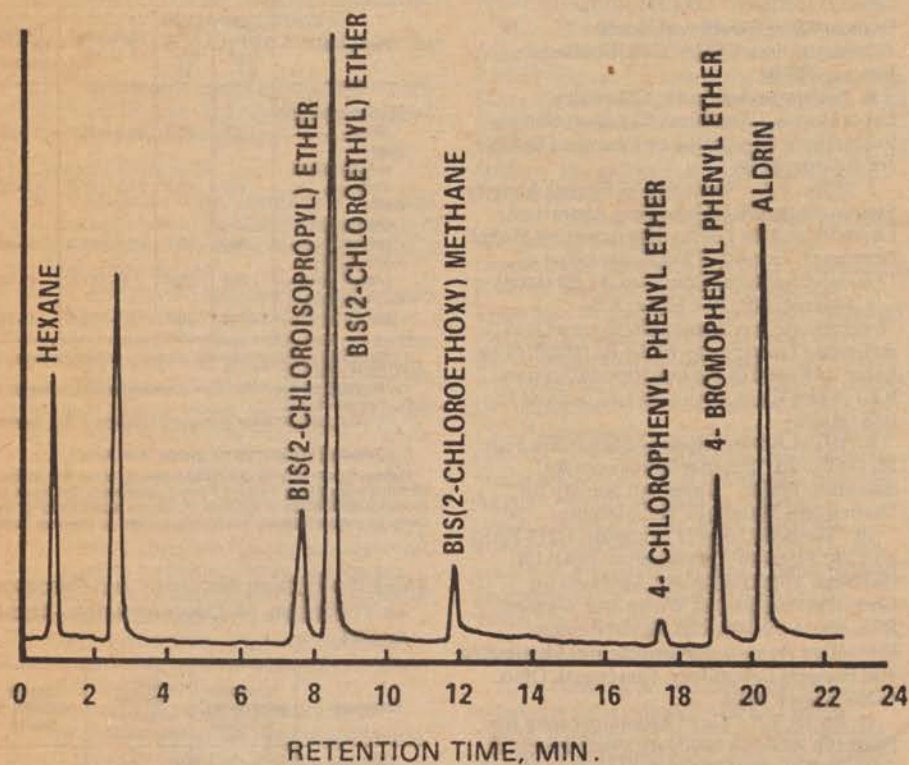


Figure 1. Gas chromatogram of haloethers.

COLUMN: TENAX GC
PROGRAM: 150°C FOR 4 MIN, 16°C/MIN TO 310°C
DETECTOR: HALL ELECTROLYTIC CONDUCTIVITY

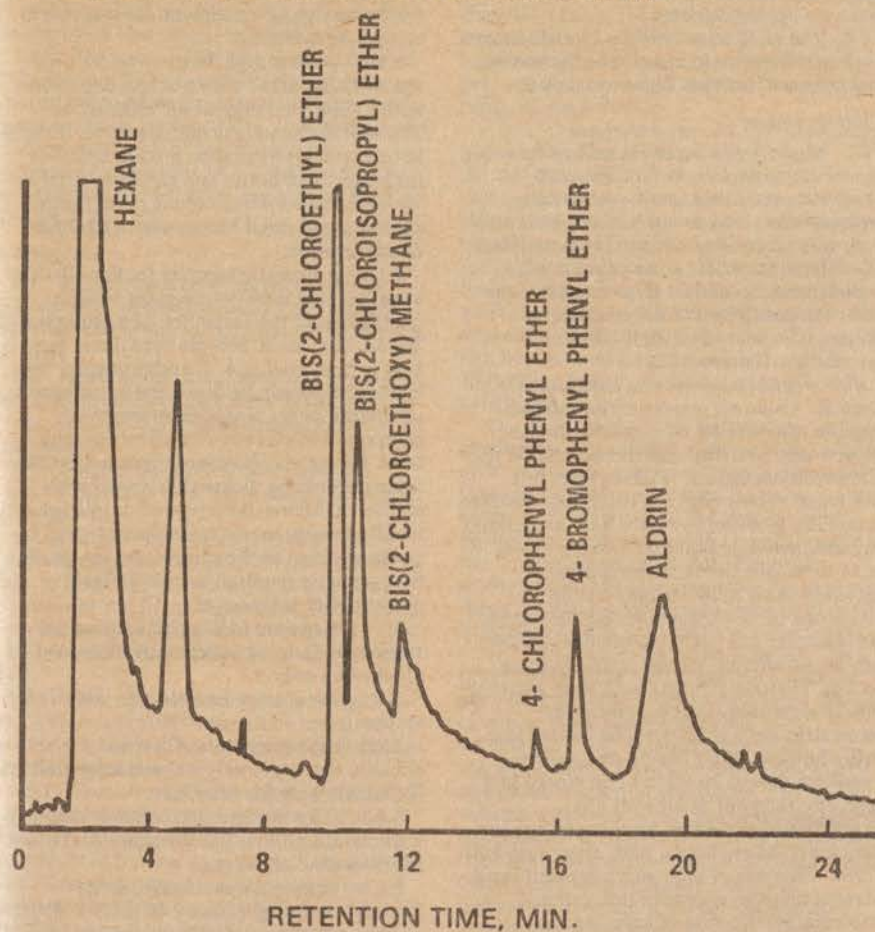


Figure 2. Gas chromatogram of haloethers.

BILLING CODE 6560-50-C

Method 612—Chlorinated Hydrocarbons

1. Scope and Application

1.1 This method covers the determination of certain chlorinated hydrocarbons. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
2-Chloronaphthalene	34581	91-58-7
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachlorocyclopentadiene	34386	77-47-4
Hexachloroethane	34396	67-72-1
1,2,4-Trichlorobenzene	34551	120-82-1

1.2 This is a gas chromatographic (GC) method applicable to the determination of the compounds listed above in municipal and industrial discharges as provided under 40 CFR 136.1. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 625 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for all of the parameters listed above, using the extract produced by this method.

1.3 The method detection limit (MDL), defined in Section 14.1¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.4 The sample extraction and concentration steps in this method are essentially the same as in Methods 606, 608, 609, and 611. Thus, a single sample may be extracted to measure the parameters included in the scope of each of these methods. When cleanup is required, the concentration levels must be high enough to permit selecting aliquots, as necessary, to apply appropriate cleanup procedures. The analyst is allowed the latitude, under Section 12, to select chromatographic conditions appropriate for the simultaneous measurement of combinations of these parameters.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is extracted with methylene chloride using a separatory funnel.

The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 mL or less. The extract is separated by gas chromatography and the parameters are then measured with an electron capture detector.²

2.2 The method provides a Florisil column cleanup procedure to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.³ Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedure in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to

laboratory safety are available and have been identified ** for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-qt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, approximately 400 mm long x 19 mm ID, with coarse frit filter disc.

5.2.3 Chromatographic column—300 long x 10 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

5.2.4 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.5 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.6 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 Gas chromatograph—An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder. A data system is recommended for measuring peak areas.

5.6.1 Column 1—1.8 m long x 2 mm ID glass, packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

Guidelines for the use of alternate column packings are provided in Section 12.1.

5.6.2 Column 2—1.8 m long $\times$ 2 mm ID glass, packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent. This column was used to develop the method performance statements in Section 14.

5.6.3 Detector—Electron capture detector. This detector has proven effective in the analysis of wastewaters for the parameters listed in the scope (Section 1.1), and was used to develop the method performance statements in Section 14. Guidelines for the use of alternate detectors are provided in Section 12.1.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Acetone, hexane, isooctane, methanol, methylene chloride, petroleum ether (boiling range 30 to 60 °C)—Pesticide quality or equivalent.

6.3 Sodium sulfate—(ACS) Granular, anhydrous. Purify heating at 400 °C for 4 h in a shallow tray.

6.4 Florisil—PR grade (60/100 mesh). Purchase activated at 1250 °F and store in the dark in glass containers with ground glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 h at 130 °C in a foil-covered glass container and allow to cool.

6.5 Stock standard solution (1.00 $\mu\text{g}/\mu\text{L}$)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.5.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in isooctane and dilute to volume in a 120-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 98% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.5.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.6 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels for

each parameter of interest by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.2.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 12 and tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to amount injected (calibration factor) is a constant over the working range (<10% relative standard deviation, RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 12 and tabulate peak height or area responses against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

C_{is} = Concentration of the internal standard ($\mu\text{g}/\text{L}$).

C_s = Concentration of the parameter to be measured ($\mu\text{g}/\text{L}$).

If the RF value over the working range is a constant (<10% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve, calibration factor, or RF must be verified on

each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that compound.

7.5 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When the results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.4, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at the following concentrations in acetone: Hexachloro-substituted parameters, 109 µg/mL; any other chlorinated hydrocarbon, 100 µg/mL. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at the test concentrations shown in Table 2 by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 2 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spike sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in

Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at the test concentration in Section 8.2.2 or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none by (2) the larger of either 5 times higher than the expected background concentration or the test concentration in Section 8.2.2.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. In necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than the test concentration in Section 8.2.2, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy ($\bar{X}$) using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 3, substituting $\bar{X}$ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}/T) \pm 2.44(100 S'/T)\%$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 2. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P-2s_p$ to $P+2s_p$. If $P=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices⁸ should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C from the time of collection until extraction.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.⁹

10. Sample Extraction

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.3 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.4 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.5 Pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.6 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 to 2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

Note.—The dichlorobenzenes have a sufficiently high volatility that significant losses may occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1 to 2 mL before removing the K-D apparatus from the hot water bath.

10.7 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Raise the temperature of the water bath to 85 to 90 °C. Concentrate the extract as in Section 10.6, except use hexane to prewet the column. The elapsed time of concentration should be 5 to 10 min.

10.8 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this

operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use the procedure below or any other appropriate procedure. However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure.

11.2 Florisil column cleanup for chlorinated hydrocarbons:

11.2.1 Adjust the sample extract to 10 mL with hexane.

11.2.2 Place 12 g of Florisil into a chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

11.2.3 Preequilibrate the column with 100 mL of petroleum ether. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons.

11.2.4 Concentrate the fraction as in Section 10.6, except use hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Analyze by gas chromatography (Section 12).

12. Gas Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by Column 2 are shown in Figures 1 and 2. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard calibration procedure is being used, the internal standard must be added to the sample extract and mixed thoroughly immediately before injection into the gas chromatograph.

12.4 Inject 2 to 5 µL of the sample extract or standard into the gas chromatograph using the solvent-flush technique.⁹ Smaller (1.0 µL)

volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 µL, the total extract volume, and the resulting peak size in area or peak height units.

12.5 Identify the parameters in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for a peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of individual compounds in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor determined in Section 7.2.2. The concentration in the sample can be calculated from Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A)(V_i)}{(V_e)(V_s)}$$

where:

A = Amount of material injected (ng).

V_i = Volume of extract injected (µL).

V_e = Volume of total extract (µL).

V_s = Volume of water extracted (mL).

13.1.2 If the internal standard calibration procedure is used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for the parameter to be measured.

A_{is} = Response for the internal standard.

I_s = Amount of internal standard added to each extract (µg).

V_o = Volume of water extracted (L).

13.2 Report results in µg/L without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹⁰ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 4×MDL to 1000×MDL.¹⁰

14.3 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 µg/L.¹¹ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

- 40 CFR Part 136, Appendix B.
- "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (In preparation).
- ASTM Annual Book of Standards, Part 31, D3694-78. "Standard Practices for Preparation of Sample Containers and for Preservation of Organic Constituents," American Society for Testing and Materials, Philadelphia.
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- "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).
- "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.
- Provost, L.P., and Elder, R.S. "Interpretation of Percent Recovery

Data," *American Laboratory*, 15, 58-63 (1983). (The value 2.44 used in the equation in Section 8.3.3 is two times the value 1.22 derived in this report.)

8. ASTM Annual Book of Standards, Part 31, D3370-76. "Standard Practices for Sampling Water," American Society for Testing and Materials, Philadelphia.

9. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," *Journal of the Association of Official Analytical Chemists*, 48, 1037 (1965).

10. "Development of Detection Limits, EPA Method 612, Chlorinated Hydrocarbons," Special letter report for EPA Contract 68-03-2625, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

11. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625 (In preparation).

12. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)		Method detection limit (µg/L)
	Column 1	Column 2	
1,3-Dichlorobenzene	4.5	6.8	1.19
Hexachloroethane	4.9	8.3	0.03
1,4-Dichlorobenzene	5.2	7.6	1.34
1,2-Dichlorobenzene	6.6	9.3	1.14
Hexachlorobutadiene	7.7	20.0	0.34
1,2,4-Trichlorobenzene	15.5	22.3	0.05
Hexachlorocyclopentadiene	nd	* 16.5	0.40
2-Chloronaphthalene	* 2.7	* 3.6	0.94
Hexachlorobenzene	* 5.6	* 10.1	0.05

Column 1 conditions: Supelcoport (100/120 mesh) coated with 1% SP-1000 packed in a 1.8 m x 2 mm ID glass column with 5% methane/95% argon carrier gas at 25 mL/min flow rate. Column temperature held isothermal at 65 °C, except where otherwise indicated.

Column 2 conditions: Supelcoport (80/100 mesh) coated with 1.5% OV-1/2.4% OV-225 packed in a 1.8 m x 2 mm ID glass column with 5% methane/95% argon carrier gas at 25 mL/min flow rate. Column temperature held isothermal at 75 °C, except where otherwise indicated.

nd = Not determined.

* 150 °C column temperature.

* 165 °C column temperature.

* 100 °C column temperature.

TABLE 2.—QC ACCEPTANCE CRITERIA—METHOD 612

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for X (µg/L)	Range for P, P _p (percent)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

X = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_p = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

NOTE.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 612

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst precision, s' (µg/L)	Overall precision, S' (µg/L)
2-Chloronaphthalene	0.75C+3.21	0.28X-1.17	0.38X-1.39
1,2-Dichlorobenzene	0.85C-0.70	0.22X-2.95	0.41X-3.92
1,3-Dichlorobenzene	0.72C+0.87	0.21X-1.03	0.49X-3.98

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 612—Continued

Parameter	Accuracy, as recovery, X' ($\mu\text{g/L}$)	Single analyst precision, s' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
1,4-Dichlorobenzene	$0.72C + 2.80$	$0.16\bar{X} - 0.48$	$0.35\bar{X} - 0.57$
Hexachlorobenzene	$0.87C - 0.02$	$0.14\bar{X} + 0.07$	$0.36\bar{X} - 0.19$
Hexachlorobutadiene	$0.61C + 0.03$	$0.18\bar{X} + 0.08$	$0.53\bar{X} - 0.12$
Hexachlorocyclopentadiene*	$0.47C$	$0.24\bar{X}$	$0.50\bar{X}$
Hexachloroethane	$0.74C - 0.02$	$0.23\bar{X} + 0.07$	$0.36\bar{X} - 0.00$
1,2,4-Trichlorobenzene	$0.76C + 0.98$	$0.23\bar{X} - 0.44$	$0.40\bar{X} - 1.37$

X' = Expected recovery for one or more measurements of a sample containing a concentration of C , in $\mu\text{g/L}$.

s' = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C , in $\mu\text{g/L}$.

* Estimates based upon the performance in a single laboratory.^{1,2}

BILLING CODE 6560-50-M

COLUMN: 1.5% OV-1/2.4% OV-225 ON SUPELCOPORT

TEMPERATURE: 75°C

DETECTOR: ELECTRON CAPTURE

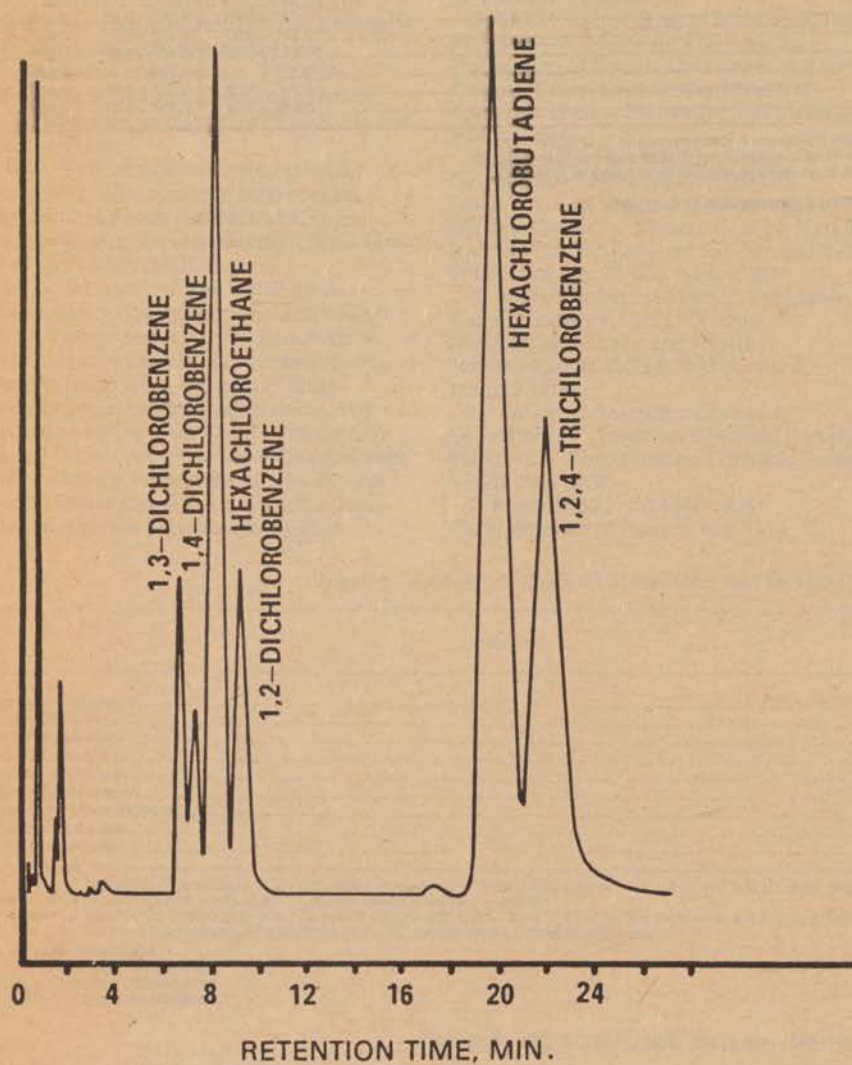


Figure 1. Gas chromatogram of chlorinated hydrocarbons.

COLUMN: 1.5% OV-1/2.4% OV-225 ON SUPELCOPORT

TEMPERATURE: 165°C

DETECTOR: ELECTRON CAPTURE

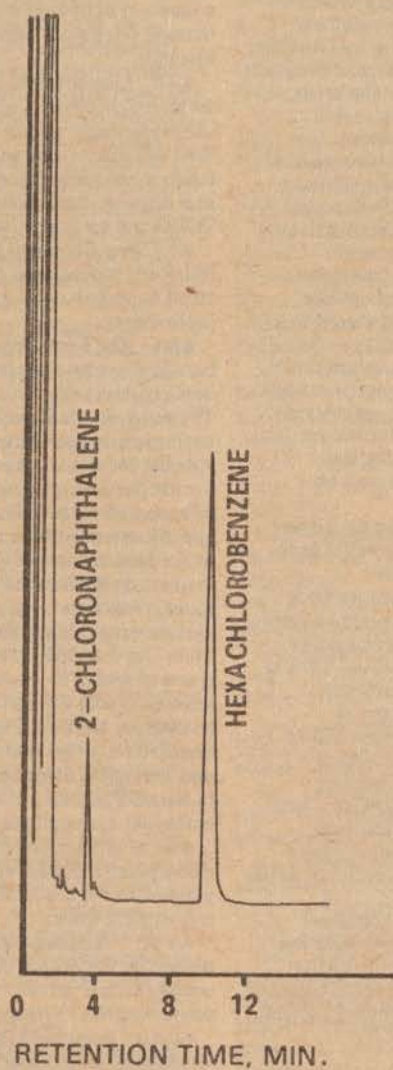


Figure 2. Gas chromatogram of chlorinated hydrocarbons.

BILLING CODE 6560-50-C

Method 613—2,3,7,8-Tetrachlorodibenzo-p-Dioxin

1. Scope and Application

1.1 This method covers the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). The following parameter may be determined by this method:

Parameter	STORET No.	GAS No.
2,3,7,8-TCDD	34675	1746-01-6

1.2 This is a gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of 2,3,7,8-TCDD in municipal and industrial discharges as provided under 40 CFR 136.1. Method 625 may be used to screen samples for 2,3,7,8-TCDD. When the screening test is positive, the final qualitative confirmation and quantification must be made using Method 613.

1.3 The method detection limit (MDL, defined in Section 14.1) for 2,3,7,8-TCDD is listed in Table 1. The MDL for a specific wastewater may be different from that listed, depending upon the nature of interferences in the sample matrix.

1.4 Because of the extreme toxicity of this compound, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain 2,3,7,8-TCDD. Section 4 of this method contains guidelines and protocols that serve as minimum safe-handling standards in a limited-access laboratory.

1.5 Any modification of this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is spiked with an internal standard of labeled 2,3,7,8-TCDD and extracted with methylene chloride using a separatory funnel. The methylene chloride extract is exchanged to hexane during concentration to a volume of 1.0 mL or less. The extract is then analyzed by capillary column GC/MS to separate and measure 2,3,7,8-TCDD.^{2,3}

2.2 The method provides selected column chromatographic cleanup procedures to aid in the elimination of interferences that may be encountered.

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the masses (m/z) monitored. All of these materials must be routinely demonstrated to be free from

interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.* Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by the treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. 2,3,7,8-TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of 2,3,7,8-TCDD. The cleanup procedures in Section 11 can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches^{1,5,7} to eliminate false positives and achieve the MDL listed in Table 1.

3.3 The primary column, SP-2330 or equivalent, resolves 2,3,7,8-TCDD from the other 21 TCDD isomers. Positive results using any other gas chromatographic column must be confirmed using the primary column.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{8,10} for the information of the analyst. Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

4.2 Each laboratory must develop a strict safety program for handling 2,3,7,8-TCDD. The following laboratory practices are recommended:

4.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

4.2.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the GC/MS should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

4.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with a wavelength greater than 290 nm for several days. (Use F 40 BL lamps or equivalent). Analyze liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

4.3 Dow Chemical U.S.A. has issued the following precautions (revised November 1978) for safe handling of 2,3,7,8-TCDD in the laboratory:

4.3.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. 2,3,7,8-TCDD is extremely toxic to laboratory animals. However, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

4.3.1.1 Protective equipment—Throw-away plastic gloves, apron or lab coat, safety glasses, and a lab hood adequate for radioactive work.

4.3.1.2 Training—Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

4.3.1.3 Personal hygiene—Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

4.3.1.4 Confinement—Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

4.3.1.5 Waste—Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in the safe handling of waste.

4.3.1.6 Disposal of wastes—2,3,7,8-TCDD decomposes above 800 °C. Low-level waste such as absorbent paper, tissues, animal remains, and plastic gloves may be burned in a good incinerator. Gross quantities (milligrams) should be packaged securely and disposed through commercial or governmental channels which are capable of handling high-level radioactive wastes or extremely toxic wastes. Liquids should be allowed to evaporate in a good hood and in a disposable container. Residues may then be handled as above.

4.3.1.7 Decontamination—For personal decontamination, use any mild soap with plenty of scrubbing action. For decontamination of glassware, tools, and surfaces, Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dishwater may be disposed to the sewer. It is prudent to minimize solvent wastes because they may require special disposal through commercial sources which are expensive.

4.3.1.8 Laundry—Clothing known to be contaminated should be disposed with the precautions described under Section 4.3.1.6. Lab coats or other clothing worn in 2,3,7,8-TCDD work areas may be laundered.

Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

4.3.1.9 Wipe tests—A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper. Extraction and analysis by gas chromatography can achieve a limit of sensitivity of 0.1 µg per wipe. Less than 1 µg of 2,3,7,8-TCDD per sample indicates acceptable cleanliness; anything higher warrants further cleaning. More than 10 µg on a wipe sample constitutes an acute hazard and requires prompt cleaning before further use of the equipment or work space. A high (> 10 µg) 2,3,7,8-TCDD level indicates that unacceptable work practices have been employed in the past.

4.3.1.10 Inhalation—Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in the case of an accident.

4.3.1.11 Accidents—Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-gal, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of

compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.1.3 Clearly label all samples as "POISON" and ship according to U.S. Department of Transportation regulations.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnels—2-L and 125-mL, with Teflon stopcock.

5.2.2 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.3 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.4 Snyder column, Kuderna-Danish—Three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.5 Snyder column, Kuderna-Danish—Two-ball micro (Kontes K-569001-0219 or equivalent).

5.2.6 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.7 Chromatographic column—300 mm long × 10 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

5.2.8 Chromatographic column—400 mm long × 11 mm ID, with Teflon stopcock and coarse frit filter disc at bottom.

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2 °C). The bath should be used in a hood.

5.5 GC/MS system:

5.5.1 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for capillary columns. Either split, splitless, or on-column injection techniques may be employed, as long as the requirements of Section 7.1.1 are achieved.

5.5.2 Column—60 m long × 0.25 mm ID glass or fused silica, coated with SP-2330 (or equivalent) with a film thickness of 0.2 µm. Any equivalent column must resolve 2, 3, 7, 8-TCDD from the other 21 TCDD isomers.¹⁶

5.5.3 Mass spectrometer—Either a low resolution mass spectrometer (LRMS) or a high resolution mass spectrometer (HRMS) may be used. The mass spectrometer must be equipped with a 70 V (nominal) ion source and be capable of acquiring m/z abundance data in real time selected ion monitoring (SIM) for groups of four or more masses.

5.5.4 GC/MS interface—Any GC to MS interface can be used that achieves the requirements of Section 7.1.1. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve

maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

5.5.5 The SIM data acquired during the chromatographic program is defined as the Selected Ion Current Profile (SICP). The SICP can be acquired under computer control or as a real time analog output. If computer control is used, there must be software available to plot the SICP and report peak height or area data for any m/z in the SICP between specified time or scan number limits.

5.6 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of 2, 3, 7, 8-TCDD.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL. Wash the solution with methylene chloride and hexane before use.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid—Concentrated (ACS, sp. gr. 1.84).

6.5 Acetone, methylene chloride, hexane, benzene, ortho-xylene, tetradecane—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Alumina—Neutral, 80/200 mesh (Fisher Scientific Co., No. A-540 or equivalent). Before use, activate for 24 h at 130 °C in a foil-covered glass container.

6.8 Silica gel—High purity grade, 100/120 mesh (Fisher Scientific Co., No. S-679 or equivalent).

6.9 Stock standard solutions (1.00 µg/µL)—Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Acetone should be used as the solvent for spiking solutions; ortho-xylene is recommended for calibration standards for split injectors; and tetradecane is recommended for splitless or on-column injectors. Analyze stock internal standards to verify the absence of native 2,3,7,8-TCDD.

6.9.1 Prepare stock standard solutions of 2,3,7,8-TCDD (mol wt 320) and either ¹³C₁₄ 2,3,7,8-TCDD (mol wt 328) or ¹³C₁₂ 2,3,7,8-TCDD (mol wt 332) in an isolated area by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality solvent and dilute to volume in a 10-mL volumetric flask. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

6.9.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store in an isolated refrigerator protected from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just

prior to preparing calibration standards or spiking solutions from them.

6.9.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

6.10 Internal standard spiking solution (25 ng/mL)—Using stock standard solution, prepare a spiking solution in acetone of either $^{13}\text{C}_{12}$ or $^{37}\text{Cl}_4$ 2,3,7,8-TCDD at a concentration of 25 ng/mL. (See Section 10.2)

6.11 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating conditions equivalent to those given in Table 1 and SIM conditions for the mass spectrometer as described in Section 12.2. The GC/MS system must be calibrated using the internal standard technique.

7.1.1 Using stock standards, prepare calibration standards that will allow measurement of relative response factors of at least three concentration ratios of 2,3,7,8-TCDD to internal standard. Each calibration standard must be prepared to contain the internal standard at a concentration of 25 ng/mL. If any interferences are contributed by the internal standard at m/z 320 and 322, its concentration may be reduced in the calibration standards and in the internal standard spiking solution (Section 6.10). One of the calibration standards should contain 2,3,7,8-TCDD at a concentration near, but above, the MDL and the other 2,3,7,8-TCDD concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 12 and tabulate peak height or area response against the concentration of 2,3,7,8-TCDD and internal standard. Calculate response factors (RF) for 2,3,7,8-TCDD using Equation 1.

Equation 1.

$$\text{RF} = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = SIM response for 2,3,7,8-TCDD m/z 320.

A_{is} = SIM response for the internal standard, m/z 332 for $^{13}\text{C}_{12}$ 2,3,7,8-TCDD m/z 328 for $^{37}\text{Cl}_4$ 2,3,7,8-TCDD.

C_{is} = Concentration of the internal standard ($\mu\text{g/L}$).

C_s = Concentration of 2,3,7,8-TCDD ($\mu\text{g/L}$).

If the RF value over the working range is a constant ($< 10\%$ relative standard deviation, RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.1.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more 2,3,7,8-TCDD calibration standards. If the response for 2,3,7,8-TCDD varies from the predicted response by more than $\pm 15\%$, the test must

be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

7.2 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.5, 11.1, and 12.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 10% of all samples with native 2,3,7,8-TCDD to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 10% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing 2,3,7,8-TCDD at a concentration of 0.100 $\mu\text{g/mL}$ in acetone. The QC check sample concentrate

must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 0.100 $\mu\text{g/L}$ (100 ng/L) by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in $\mu\text{g/L}$, and the standard deviation of the recovery (s) in $\mu\text{g/L}$, for 2,3,7,8-TCDD using the four results.

8.2.5 Compare s and ($\bar{X}$) with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 2. If s and $\bar{X}$ meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If s exceeds the precision limit or $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for 2,3,7,8-TCDD. Locate and correct the source of the problem and repeat the test beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 10% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of 2,3,7,8-TCDD in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of 2,3,7,8-TCDD in the sample is not being checked against a limit specific to that parameter, the spike should be at 0.100 $\mu\text{g/L}$ or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 0.100 $\mu\text{g/L}$.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of 2,3,7,8-TCDD. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the

concentration after spiking (A) of 2,3,7,8-TCDD. Calculate percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for 2,3,7,8-TCDD with the corresponding QC acceptance criteria found in Table 2. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.¹¹ If spiking was performed at a concentration lower than 0.100 µg/L, the analyst must use either the QC acceptance criteria in Table 2, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of 2,3,7,8-TCDD: (1) calculate accuracy (X') using the equation in Table 3, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 3, substituting X' for X; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) \pm 2.44(100 S'/T)\%$.¹¹

8.3.4 If the recovery of 2,3,7,8-TCDD falls outside the designated range for recovery, a check standard must be analyzed as described in Section 8.4.

8.4 If the recovery of 2,3,7,8-TCDD fails the acceptance criteria for recovery in Section 8.3, a QC check standard must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the complexity of the sample matrix and the performance of the laboratory.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Section 8.2.1 or 8.3.2) to 1 L of reagent water.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of 2,3,7,8-TCDD. Calculate the percent recovery (P_a) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_a) with the corresponding QC acceptance criteria found in Table 2. If the recovery of 2,3,7,8-TCDD falls outside the designated range, the laboratory performance is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for 2,3,7,8-TCDD in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery (P) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P-2s_p$ to $P+2s_p$. If $P=90\%$ and $s_p=10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method.

The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices¹² should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All samples must be iced or refrigerated at 4 °C and protected from light from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.¹³ Field test kits are available for this purpose.

9.3 Label all samples and containers "POISON" and ship according to applicable U.S. Department of Transportation regulations.

9.4 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.²

10. Sample Extraction

Caution: When using this method to analyze for 2,3,7,8-TCDD, all of the following operations must be performed in a limited-access laboratory with the analyst wearing full protective covering for all exposed skin surfaces. See Section 4.2.

10.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel.

10.2 Add 1.00 mL of internal standard spiking solution to the sample in the separatory funnel. If the final extract will be concentrated to a fixed volume below 1.00 mL (Section 12.3), only that volume of spiking solution should be added to the sample so that the final extract will contain 25 ng/mL of internal standard at the time of analysis.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.5 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.6 Pour the combined extract into the K-D concentrator. Rinse the Erlenmeyer flask with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.7 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.8 Momentarily remove the Snyder column, add 50 mL of hexane and a new boiling chip, and reattach the Snyder column. Raise the temperature of the water bath to 85 to 90 °C. Concentrate the extract as in Section 10.7, except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of hexane. A 5-mL syringe is recommended for this operation. Set aside the K-D glassware for reuse in Section 10.14.

10.9 Pour the hexane extract from the concentrator tube into a 125-mL separatory funnel. Rinse the concentrator tube four times with 10-mL aliquots of hexane. Combine all rinses in the 125-mL separatory funnel.

10.10 Add 50 mL of sodium hydroxide solution to the funnel and shake for 30 to 60 s. Discard the aqueous phase.

10.11 Perform a second wash of the organic layer with 50 mL of reagent water. Discard the aqueous phase.

10.12 Wash the hexane layer with a least two 50-mL aliquots of concentrated sulfuric acid. Continue washing the hexane layer with 50-mL aliquots of concentrated sulfuric acid until the acid layer remains colorless. Discard all acid fractions.

10.13 Wash the hexane layer with two 50-mL aliquots of reagent water. Discard the aqueous phases.

10.14 Transfer the hexane extract into a 125-mL Erlenmeyer flask containing 1 to 2 g of anhydrous sodium sulfate. Swirl the flask for 30 s and decant the hexane extract into the reassembled K-D apparatus. Complete the quantitative transfer with two 10-mL hexane rinses of the Erlenmeyer flask.

10.15 Replace the one or two clean boiling chips and concentrate the extract to 6 to 10 mL as in Section 10.8.

10.16 Add a clean boiling chip to the concentrator tube and attach a two-ball micro-Snyder column. Prewet the column by adding about 1 mL of hexane to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 mL of hexane.

Adjust the extract volume to 1.0 mL with hexane. Stopper the concentrator tube and store refrigerated and protected from light if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with GC/MS analysis (Section 12). If the sample requires further cleanup, proceed to Section 11.

10.17 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst may use either procedure below or any other appropriate procedure.¹⁻⁷ However, the analyst first must demonstrate that the requirements of Section 8.2 can be met using the method as revised to incorporate the cleanup procedure. Two cleanup column options are offered to the analyst in this section. The alumina column should be used first to overcome interferences. If background problems are still encountered, the silica gel column may be helpful.

11.2 Alumina column cleanup for 2,3,7,8-TCDD:

11.2.1 Fill a 300 mm long x 10 mm ID chromatographic column with activated alumina to the 150 mm level. Tap the column gently to settle the alumina and add 10 mm of anhydrous sodium sulfate to the top.

11.2.2 Preequilibrate the column with 50 mL of hexane. Adjust the elution rate to 1 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1.0-mL sample extract onto the column using two 2-mL portions of hexane to complete the transfer.

11.2.3 Just prior to exposure of the sodium sulfate layer to the air, add 50 mL of 3% methylene chloride/97% hexane (V/V) and continue the elution of the column. Discard the eluate.

11.2.4 Next, elute the column with 50 mL of 20% methylene chloride/80% hexane (V/V) into a 500-mL K-D flask equipped with a 10-

mL concentrator tube. Concentrate the collected fraction to 1.0 mL as in Section 10.16 and analyze by GC/MS (Section 12).

11.3 Silica gel column cleanup for 2,3,7,8-TCDD:

11.3.1 Fill a 400 mm long x 11 mm ID chromatographic column with silica gel to the 300 mm level. Tap the column gently to settle the silica gel and add 10 mm of anhydrous sodium sulfate to the top.

11.3.2 Preequilibrate the column with 50 mL of 20% benzene/80% hexane (V/V). Adjust the elution rate to 1 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 1.0-mL sample extract onto the column using two 2-mL portions of 20% benzene/80% hexane to complete the transfer.

11.3.3 Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of 20% benzene/80% hexane to the column. Collect the eluate in a clean 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction to 1.0 mL as in Section 10.16 and analyze by GC/MS.

12. GC/MS Analysis

12.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. Other capillary columns or chromatographic conditions may be used if the requirements of Sections 5.5.2 and 8.2 are met.

12.2 Analyze standards and samples with the mass spectrometer operating in the selected ion monitoring (SIM) mode using a dwell time to give at least seven points per peak. For LRMS, use masses at m/z 320, 322, and 257 for 2,3,7,8-TCDD and either m/z 328 for ^{37}Cl , 2,3,7,8-TCDD or m/z 332 for $^{13}\text{C}_{12}$, 2,3,7,8-TCDD. For HRMS, use masses at m/z 319.8965 and 321.8936 for 2,3,7,8-TCDD and either m/z 327.8847 for ^{37}Cl , 2,3,7,8-TCDD or m/z 331.9367 for $^{13}\text{C}_{12}$, 2,3,7,8-TCDD.

12.3 If lower detection limits are required, the extract may be carefully evaporated to dryness under a gentle stream of nitrogen with the concentrator tube in a water bath at about 40 °C. Conduct this operation immediately before GC/MS analysis. Redissolve the extract in the desired final volume of ortho-xylene or tetradecane.

12.4 Calibrate the system daily as described in Section 7.

12.5 Inject 2 to 5 μL of the sample extract into the gas chromatograph. The volume of calibration standard injected must be measured, or be the same as all sample injection volumes.

12.6 The presence of 2,3,7,8-TCDD is qualitatively confirmed if all of the following criteria are achieved:

12.6.1 The gas chromatographic column must resolve 2,3,7,8-TCDD from the other 21 TCDD isomers.

12.6.2 The masses for native 2,3,7,8-TCDD (LRMS- m/z 320, 322, and 257 and HRMS- m/z 320 and 322) and labeled 2,3,7,8-TCDD (m/z 328 or 332) must exhibit a simultaneous maximum at a retention time that matches that of native 2,3,7,8-TCDD in the calibration standard, with the performance specifications of the analytical system.

12.6.3 The chlorine isotope ratio at m/z 320 and m/z 322 must agree to within $\pm 10\%$ of that in the calibration standard.

12.6.4 The signal of all peaks must be greater than 2.5 times the noise level.

12.7 For quantitation, measure the response of the m/z 320 peak for 2,3,7,8-TCDD and the m/z 332 peak for $^{13}\text{C}_{12}$, 2,3,7,8-TCDD or the m/z 328 peak for ^{37}Cl , 2,3,7,8-TCDD.

12.8 Co-eluting impurities are suspected if all criteria are achieved except those in Section 12.6.3. In this case, another SIM analysis using masses at m/z 257, 259, 320 and either m/z 328 or m/z 332 can be performed. The masses at m/z 257 and m/z 259 are indicative of the loss of one chlorine and one carbonyl group from 2,3,7,8-TCDD. If masses m/z 257 and m/z 259 give a chlorine isotope ratio that agrees to within $\pm 10\%$ of the same cluster in the calibration standards, then the presence of TCDD can be confirmed. Co-eluting DDD, DDE, and PCB residues can be confirmed, but will require another injection using the appropriate SIM masses or full repetitive mass scans. If the response for ^{37}Cl , 2,3,7,8-TCDD at m/z 328 is too large, PCB contamination is suspected and can be confirmed by examining the response at both m/z 326 and m/z 328. The ^{37}Cl , 2,3,7,8-TCDD internal standard gives negligible response at m/z 326. These pesticide residues can be removed using the alumina column cleanup procedure.

12.9 If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst should employ additional cleanup procedures and reanalyze by GC/MS.

12.10 In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry is suggested.⁸

13. Calculations

13.1 Calculate the concentration of 2,3,7,8-TCDD in the sample using the response factor (RF) determined in Section 7.1.2 and Equation 2.

Equation 2:

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(\text{RF})(V_o)}$$

where:

A_s = SIM response for 2,3,7,8-TCDD at m/z 320.

A_{is} = SIM response for the internal standard at m/z 328 or 332.

I_s = Amount of internal standard added to each extract (μg).

V_o = Volume of water extracted (L).

13.2 For each sample, calculate the percent recovery of the internal standard by comparing the area of the m/z peak measured in the sample to the area of the same peak in the calibration standard. If the recovery is below 50%, the analyst should review all aspects of his analytical technique.

13.3 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data

obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentration listed in Table 1 was obtained using reagent water.¹⁴ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 11 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.02 to 0.20 µg/L.¹⁵ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 3.

References

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Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, March 1979.

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TABLE 1.—Chromatographic Conditions and Method Detection Limit

Parameter	Retention time (min)	Method detection limit (µg/L)
2,3,7,8-TCDD	13.1	0.002

Column conditions: SP-2330 coated on a 60 m long x 0.25 mm ID glass column with hydrogen carrier gas at 40 cm/sec linear velocity, splitless injection using tetradecane. Column temperature held isothermal at 200°C for 1 min, then programmed at 8°C/min to 250°C and held. Use of helium carrier gas will approximately double the retention time.

TABLE 2.—QC Acceptance Criteria—Method 613

Parameter	Test conc. (µg/L)	Limit for s (µg/L)	Range for X (µg/L)	Range for P, P _s (%)
2,3,7,8-TCDD	0.100	0.0276	0.0523-0.1226	45-129

s = Standard deviation of four recovery measurements, in µg/L (Section 8.2.4).

X = Average recovery for four recovery measurements, in µg/L (Section 8.2.4).

P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

Note.—These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 613

Parameter	Accuracy, as recovery, X' (µg/L)	Single analyst, precision, s _s (µ/L)	Overall precision, S (µg/L)
2,3,7,8-TCDD	0.86C + 0.00145	0.13X̄ + 0.00129	0.19X̄ + 0.00028

X' = Expected recovery for one or more measurements, of a sample containing a concentration of C, in µg/L.

s_s = Expected single analyst standard deviation of measurements at an average concentration found of X̄, in µg/L.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of X̄, in µg/L.

C = True value for the concentration, in µg/L.

X̄ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.

Method 624—Purgeables

1. Scope and Application

1.1 This method covers the determination of a number of purgeable organics. The following parameters may be determined by this method:

Parameter	STORET No.	CAS No.
Benzene	34030	71-43-2
Bromodichloromethane	32101	75-27-4
Bromodiform	32104	75-25-2
Bromomethane	34413	74-83-9
Carbon tetrachloride	32102	56-23-5
Chlorobenzene	34301	108-90-7
Chloroethane	34311	75-00-3
2-Chloroethylvinyl ether	34576	110-75-6
Chloroform	32106	67-66-3

Parameter	STORET No.	CAS No.
Chloromethane	34418	74-87-3
Dibromochloromethane	32105	124-48-1
1,2-Dichlorobenzene	34536	95-50-1
1,3-Dichlorobenzene	34566	541-73-1
1,4-Dichlorobenzene	34571	106-46-7
1,1-Dichloroethane	34496	75-34-3
1,2-Dichloroethane	34531	107-06-2
1,1-Dichloroethane	34501	75-35-4
trans-1,2-Dichloroethane	34546	156-60-5
1,2-Dichloropropane	34541	78-87-5
cis-1,3-Dichloropropane	34704	10061-01-5
trans-1,3-Dichloropropane	34699	10061-02-6
Ethyl benzene	34371	100-41-4
Methylene chloride	34423	75-09-2
1,1,2,2-Tetrachloroethane	34516	79-34-5
Tetrachloroethene	34475	127-18-4
Toluene	34010	108-88-3
1,1,1-Trichloroethane	34506	71-55-6
1,1,2-Trichloroethane	34511	79-00-5

Parameter	STORET No.	CAS No.
Trichloroethane	39180	79-01-6
Trichlorofluoromethane	34488	75-69-4
Vinyl chloride	39175	75-01-4

1.2 The method may be extended to screen samples for acrolein (STORET No. 34210, CAS No. 107-02-8) and acrylonitrile (STORET No. 34215, CAS No. 107-13-1), however, the preferred method for these two compounds in Method 603.

1.3 This is a purge and trap gas chromatographic/mass spectrometer (GC/MS) method applicable to the determination of the compounds listed above in municipal

and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 14.1)¹ for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the operation of a purge and trap system and a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 An inert gas is bubbled through a 5-mL water sample contained in a specially-designed purging chamber at ambient temperature. The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.^{2,3}

3. Interferences

3.1 Impurities in the purge gas, organic compounds outgassing from the plumbing ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3. The use of non-Teflon plastic tubing, non-Teflon thread sealants, or flow controllers with rubber components in the purge and trap system should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal into the sample during shipment and storage. A field reagent blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Contamination by carry-over can occur whenever high level and low level samples are sequentially analyzed. To reduce carry-over, the purging device and sample syringe must be rinsed with reagent water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an

analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high purgeable levels, it may be necessary to wash the purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105 °C oven between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified^{4,5} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete sampling.

5.1.1 Vial—25-mL capacity or larger, equipped with a screw cap with a hole in the center (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C before use.

5.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled water, and dry at 105 °C for 1 h before use.

5.2 Purge and trap system—The purge and trap system consists of three separate pieces of equipment: a purging device, trap, and desorber. Several complete systems are now commercially available.

5.2.1 The purging device must be designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging device illustrated in Figure 1 meets these design criteria.

5.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. The trap must be packed to contain the

following minimum lengths of adsorbents: 1.0 cm of methyl silicone coated packing (Section 6.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 6.3.1), and 8 cm of silica gel (Section 6.3.3). The minimum specifications for the trap are illustrated in Figure 2.

5.2.3 The desorber should be capable of rapidly heating the trap to 180 °C. The polymer section of the trap should not be heated higher than 180 °C and the remaining sections should not exceed 200 °C. The desorber illustrated in Figure 2 meets these design criteria.

5.2.4 The purge and trap system may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 3 and 4.

5.3 GC/MS system:

5.3.1 Gas chromatograph—An analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, and gases.

5.3.2 Column—6 ft long x 0.1 in ID stainless steel or glass, packed with 1% SP-1000 on Carbowax B (60/80 mesh) or equivalent. This column was used to develop the method performance statements in Section 14. Guidelines for the use of alternate column packings are provided in Section 11.1.

5.3.3 Mass spectrometer—Capable of scanning from 20 to 260 amu every 7 s or less, utilizing 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 2 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet.

5.3.4 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 10) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.3.5 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific m/z (masses) and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

5.4 Syringes—5-mL, glass hypodermic with Luerlok tip (two each), if applicable to the purging device.

5.5 Micro syringes—25-μL, 0.006 in. ID needle.

5.6 Syringe valve—2-way, with Luer ends (three each).

5.7 Syringe—5-mL, gas-tight with shut-off valve.

5.8 Bottle—15-mL, screw-cap, with Teflon cap liner.

5.9 Balance—Analytical, capable of accurately weighing 0.0001 g.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.1.1 Reagent water can be generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon (Filtrisorb-300, Calgon Corp., or equivalent).

6.1.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate reagent water.

6.1.3 Reagent water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90 °C, bubble a contaminant-free inert gas through the water for 1 h. While still hot, transfer the water to a narrow mouth screw-cap bottle and seal with a Teflon-lined septum and cap.

6.2 Sodium thiosulfate—(ACS) Granular.

6.3 Trap materials:

6.3.1 2,6-Diphenylene oxide polymer—Tenax, (60/80 mesh), chromatographic grade or equivalent.

6.3.2 Methyl silicone packing—3% OV-1 on Chromosorb-W (60/80 mesh) or equivalent.

6.3.3 Silica gel—35/60 mesh, Davison, grade-15 or equivalent.

6.4 Methanol—Pesticide quality or equivalent.

6.5 Stock standard solutions—Stock standard solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the compounds, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

6.5.1 Place about 9.8 mL of methanol into a 10-mL ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

6.5.2 Add the assayed reference material:

6.5.2.1 Liquids—Using a 100-μL syringe, immediately add two or more drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

6.5.2.2 Gases—To prepare standards for any of the four halocarbons that boil below 30 °C (bromomethane, chloroethane, chloromethane, and vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve in the methanol).

6.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in μg/μL from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to

calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.5.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at -10 to -20 °C and protect from light.

6.5.5 Prepare fresh standards weekly for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

6.6 Secondary dilution standards—Using stock solutions, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 7.3 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 3. Prepare stock standard solutions for each surrogate standard in methanol as described in Section 6.5. Prepare a surrogate standard spiking solution from these stock standards at a concentration of 15 μg/mL in water. Store the solutions at 4 °C in Teflon-sealed glass containers with a minimum of headspace. The solutions should be checked frequently for stability. The addition of 10 μL of this solution of 5 mL of sample or standard is equivalent to a concentration of 30 μg/L of each surrogate standard.

6.8 BFB Standard—Prepare a 25 μg/mL solution of BFB in methanol.

6.9 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Assemble a purge and trap system that meets the specifications in Section 5.2. Condition the trap overnight at 180 °C by backflushing with an inert gas flow of at least 20 mL/min. Condition the trap for 10 min once daily prior to use.

7.2 Connect the purge and trap system to a gas chromatograph. The gas chromatograph must be operated using temperature and flow rate conditions equivalent to those given in Table 1.

7.3 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 3.

7.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 μL of one or more secondary dilution standards to 50, 250, or 500 mL of reagent water. A 25-μL

syringe with a 0.006 in. ID needle should be used for this operation. One of the calibration standards should be at a concentration near, but above, the MDL (Table 1) and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system. These aqueous standards can be stored up to 24 h, if held in sealed vials with zero headspace as described in Section 9.2. If not so stored, they must be discarded after 1 h.

7.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 6.5 and 6.6. It is recommended that the secondary dilution standard be prepared at a concentration of 15 μg/mL of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 μg/L.

7.3.3 Analyze each calibration standard according to Section 11, adding 10 μL of internal standard spiking solution directly to the syringe (Section 11.4). Tabulate the area response of the characteristic m/z against concentration for each compound and internal standard, and calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$RF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard.

C_s = Concentration of the parameter to be measured.

If the RF value over the working range is a constant (<35% RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.4 The working calibration curve or RF must be verified on each working day by the measurement of a QC check sample.

7.4.1 Prepare the QC check sample as described in Section 8.2.2.

7.4.2 Analyze the QC check sample according to the method beginning in Section 10.

7.4.3 For each parameter, compare the response (Q) with the corresponding calibration acceptance criteria found in Table 5. If the responses for all parameters of interest fall within the designated ranges, analysis of actual samples can begin. If any individual Q falls outside the range, proceed according to Section 7.4.4.

Note.—The large number of parameters in Table 5 present a substantial probability that one or more will not meet the calibration

acceptance criteria when all parameters are analyzed.

7.4.4 Repeat the test only for those parameters that failed to meet the calibration acceptance criteria. If the response for a parameter does not fall within the range in this second test, a new calibration curve or RF must be prepared for that parameter according to Section 7.3.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Section 11.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Each day, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system are under control.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must spike all samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.5.

8.1.7 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.6.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 10

μg/mL in methanol. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2 Prepare a QC check sample to contain 20 μg/L of each parameter by adding 200 μL of QC check sample concentrate to 100 mL of reagent water.

8.2.3 Analyze four 5-mL aliquots of the well-mixed QC check sample according to the method beginning in Section 10.

8.2.4 Calculate the average recovery ($\bar{X}$) in μg/L, and the standard deviation of the recovery (s) in μg/L, for each parameter of interest using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 5. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 5 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.3.

8.2.6.2 Beginning with Section 8.2.3, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.3.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 20 μg/L or 1 to 5 times

higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second 5-mL sample aliquot with 10 μL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 5. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 μg/L, the analyst must use either the QC acceptance criteria in Table 5, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy (X') using the equation in Table 6, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 6, substituting X' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 X'/T) (\pm 2.44(100 S'/T)\%)$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of parameters in Table 5 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.4.1 Prepare the QC check standard by adding 10 μL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 5 mL of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 5.

Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solutions as described in Section 11.4, and calculate the percent recovery of each surrogate compound.

8.6 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter a regular basis (e.g. after each five to ten new accuracy measurements).

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 All samples must be iced or refrigerated from the time of collection until analysis. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL is sufficient for up to 5 ppm Cl_2) to the empty sample bottle just prior to shipping to the sampling site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.* Field test kits are available for this purpose.

9.2 Grab samples must be collected in glass containers having a total volume of at least 25 mL. Fill the sample bottle just to overflowing in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. If preservative has been added, shake vigorously for 1 min. Maintain the hermetic seal on the sample bottle until time of analysis.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions.³ Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be

determined. Collect about 500 mL of sample in a clean container. Adjust the pH of the sample to about 2 by adding 1+1 HCl while stirring vigorously. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in Section 9.2.

9.4 All samples must be analyzed within 14 days of collection.³

10. Daily GC/MS Performance Tests

10.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for BFB.⁹ The performance test must be passed before any samples, blanks, or standards are analyzed, unless the instrument has met the DFTPP test described in Method 625 earlier in the day.¹⁰

10.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)

Mass Range: 20 to 260 amu

Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

10.3 At the beginning of each day, inject 2 μL of BFB solution directly on the column. Alternatively, add 2 μL of BFB solution to 5.0 mL of reagent water or standard solution and analyze the solution according to section 11. Obtain a background-corrected mass spectrum of BFB and confirm that all the key m/z criteria in Table 2 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved.

11. Sample Purging and Gas Chromatography

11.1 Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and MDL that can be achieved under these conditions. An example of the separations achieved by this column is shown in Figure 5. Other packed columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

11.2 After achieving the key m/z abundance criteria in Section 10, calibrate the system daily as described in Section 7.

11.3 Adjust the purge gas (helium) flow rate to 40 mL/min. Attach the trap inlet to the purging device, and set the purge and trap system to purge (Figure 3). Open the syringe valve located on the purging device sample introduction needle.

11.4 Allow the sample to come to ambient temperature prior to introducing it into the syringe. Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 10.0 μL of the surrogate spiking solution (Section 6.7) and 10.0 μL of the internal standard spiking solution (Section 7.3.2) through the valve bore, then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution.

11.5 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

11.6 Close both valves and purge the sample for 11.0 ± 0.1 min at ambient temperature.

11.7 After the 11-min purge time, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4), and begin to temperature program the gas chromatograph. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 mL/min for 4 min. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30°C (subambient temperature, if problems persist) instead of the initial program temperature of 45°C .

11.8 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL flushes of reagent water.

11.9 After desorbing the sample for 4 min, recondition the trap by returning the purge and trap system to the purge mode. Wait 15 s then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C . After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

11.10 If the response for any m/z exceeds the working range of the system, prepare a dilution of the sample with reagent water from the aliquot in the second syringe and reanalyze.

12. Qualitative Identification

12.1 Obtain EICPs for the primary m/z (Table 4) and at least two secondary masses for each parameter of interest. The following criteria must be met to make a qualitative identification:

12.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

12.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

12.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within $\pm 20\%$ of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

12.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

13. Calculations

13.1 When a parameter has been identified, the quantitation of that parameter should be based on the integrated abundance

from the EICP of the primary characteristic m/z given in Table 4. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.3 and Equation 2.

Equation 2.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(C_{is})}{(A_{is})(\text{RF})}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard.

13.2 Report results in $\mu\text{g/L}$ without correction for recovery data. All QC data obtained should be reported with the sample results.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Table 1 were obtained using reagent water.¹¹ Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

14.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5–800 $\mu\text{g/L}$.¹² Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 5.

References

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TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)
Chloromethane	2.3	nd
Bromomethane	3.1	nd
Vinyl chloride	3.8	nd
Chloroethane	4.8	nd
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	nd
1,1-Dichloroethane	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethane	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
cis-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
trans-1,3-Dichloropropene	17.2	nd
2-Chloroethylvinyl ether	18.6	nd
Bromotoluene	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1

TABLE 1.—CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS—Continued

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	nd
1,2-Dichlorobenzene	35.0	nd
1,4-Dichlorobenzene	35.4	nd

Column conditions: Carbowax B (60/80 mesh) coated with 1% SP-1000 packed in a 6 ft by 0.1 in. ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held at 45°C for 3 min, then programmed at 8°C/min to 220°C and held for 15 min.
nd—not determined.

TABLE 2.—BFB KEY M/Z ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
50	15 to 40% of mass 95.
75	30 to 60% of mass 95.
95	Base Peak, 100% Relative Abundance.
96	5 to 9% of mass 95.
173	<2% of mass 174.
174	>50% of mass 95.
175	5 to 9% of mass 174.
176	>95% but < 101% of mass 174.
177	5 to 9% of mass 176.

TABLE 3.—SUGGESTED SURROGATE AND INTERNAL STANDARDS

Compound	Retention time (min)*	Primary m/z	Secondary masses
Benzene d-6	17.0	84	
4-Bromofluorobenzene	28.3	95	174, 176
1,2-Dichloroethane d-4	12.1	102	
1,4-Difluorobenzene	19.6	114	63, 86
Ethylbenzene d-5	26.4	111	
Ethylbenzene d-10	26.4	98	
Fluorobenzene	18.4	96	70
Pentafluorobenzene	23.5	168	
Bromochloromethane	9.3	128	49, 130, 51
2-Bromo-1-chloropropane	19.2	77	79, 156
1, 4-Dichlorobutane	25.8	55	90, 92

*For chromatographic conditions, see Table 1.

TABLE 4.—CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS

Parameter	Primary	Secondary
Chloromethane	50	52
Bromomethane	94	96
Vinyl chloride	62	64
Chloroethane	64	66
Methylene chloride	84	49, 51, and 86
Trichlorofluoromethane	101	103
1,1-Dichloroethane	96	61 and 98
1,1-Dichloroethane	63	65, 83, 85, 86, and 100
trans-1,2-Dichloroethane	96	61 and 98
Chloroform	83	85
1,2-Dichloroethane	98	62, 64, and 100
1,1,1-Trichloroethane	97	99, 117, and 119
Carbon tetrachloride	117	119 and 121
Bromodichloromethane	127	83, 85, and 129
1,2-Dichloropropane	112	63, 65, and 114
trans-1,3-Dichloropropene	75	77
Trichloroethene	130	95, 97, and 132
Benzene	78	
Dibromochloromethane	127	129, 208, and 206
1,1,2-Trichloroethane	97	83, 85, 99, 132, and 134
cis-1,3-Dichloropropene	75	77
2-Chloroethylvinyl ether	106	63 and 65

TABLE 4.—CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
Bromoform.....	173	171, 175, 250, 252, 254, and 256.
1,1,2,2-Tetrachloroethane.....	168	83, 85, 131, 133, and 166.

TABLE 4.—CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
Tetrachloroethene.....	164	129, 131, and 166.
Toluene.....	92	91.
Chlorobenzene.....	112	114.
Ethyl benzene.....	106	91.

TABLE 4.—CHARACTERISTIC MASSES FOR PURGEABLE ORGANICS—Continued

Parameter	Primary	Secondary
1,3-Dichlorobenzene.....	146	148 and 113.
1,2-Dichlorobenzene.....	146	148 and 113.
1,4-Dichlorobenzene.....	146	148 and 113.

TABLE 5.—CALIBRATION AND QC ACCEPTANCE CRITERIA—METHOD 624*

Parameter	Range for Q (μ /g/L)	Limit for s (μ /g/L)	Range for $\bar{X}$ (μ /g/L)	Range for P, P _s (%)
Benzene.....	12.8–27.2	6.9	15.2–26.0	37–151
Bromodichloromethane.....	13.1–26.9	6.4	10.1–28.0	35–155
Bromoform.....	14.2–25.8	5.4	11.4–31.1	45–169
Bromomethane.....	2.8–37.2	17.9	D–41.2	D–242
Carbon tetrachloride.....	14.6–25.4	5.2	17.2–23.5	70–140
Chlorobenzene.....	13.2–26.8	6.3	16.4–27.4	37–160
Chloroethane.....	7.6–32.4	11.4	8.4–40.4	14–230
2-Chloroethylvinyl ether.....	D–44.8	25.9	D–50.4	D–305
Chloroform.....	13.5–26.5	6.1	13.7–24.2	51–138
Chloromethane.....	D–40.8	19.8	D–45.9	D–273
Dibromochloromethane.....	13.5–26.5	6.1	13.8–26.6	53–149
1,2-Dichlorobenzene.....	12.6–27.4	7.1	11.8–34.7	18–190
1,3-Dichlorobenzene.....	14.6–25.4	5.5	17.0–28.8	59–156
1,4-Dichlorobenzene.....	12.6–27.4	7.1	11.8–34.7	18–190
1,1-Dichloroethane.....	14.5–25.5	5.1	14.2–28.5	59–155
1,2-Dichloroethane.....	13.6–26.4	6.0	14.3–27.4	49–155
1,1-Dichloroethene.....	10.1–29.9	9.1	3.7–42.3	D–234
trans-1,2-Dichloroethene.....	13.9–26.1	5.7	13.6–28.5	54–156
1,2-Dichloropropane.....	6.8–33.2	13.8	3.8–36.2	D–210
cis-1,3-Dichloropropene.....	4.8–35.2	15.8	1.0–39.0	D–227
trans-1,3-Dichloropropene.....	10.0–30.0	10.4	7.6–32.4	17–183
Ethyl benzene.....	11.8–28.2	7.5	17.4–26.7	37–162
Methylene chloride.....	12.1–27.9	7.4	D–41.0	D–221
1,1,2,2-Tetrachloroethane.....	12.1–27.9	7.4	13.5–27.2	46–157
Tetrachloroethene.....	14.7–25.3	5.0	17.0–26.6	64–148
Toluene.....	14.9–25.1	4.8	16.6–26.7	47–162
1,1,1-Trichloroethane.....	15.0–25.0	4.6	13.7–30.1	52–162
1,1,2-Trichloroethane.....	14.2–25.8	5.5	14.3–27.1	52–150
Trichloroethane.....	13.3–26.7	6.6	16.6–27.6	71–157
Trichlorofluoromethane.....	9.6–30.4	10.0	8.9–31.5	17–181
Vinyl chloride.....	0.8–39.2	20.0	D–43.5	D–251

Q=Concentration measured in QC check sample, in μ g/L (Section 7.5.3).s=Standard deviation of four recovery measurements, in μ g/L (Section 8.2.4). $\bar{X}$ =Average recovery of four recovery measurements, in μ g/L (Section 8.2.4).P, P_s=Percent recovery measured, (Section 8.3.2, Section 8.4.2).

D=Detected; result must be greater than zero.

*Criteria were calculated assuming a QC check sample concentration of 20 μ g/L.

NOTE.—These criteria are based directly upon the method performance data in Table 6. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 6.

TABLE 6.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 624

Parameter	Accuracy, as recovery, $\bar{X}$ (μ g/L)	Single analyst precision, s _a (μ g/L)	Overall precision, S _t (μ g/L)
Benzene.....	0.93C+2.00	0.26 $\bar{X}$ –1.74	0.25 $\bar{X}$ –1.33
Bromodichloromethane.....	1.03C–1.58	0.15 $\bar{X}$ +0.59	0.20 $\bar{X}$ +1.13
Bromoform.....	1.18C–2.35	0.12 $\bar{X}$ +0.34	0.17 $\bar{X}$ +1.38
Bromomethane.....	1.00C	0.43 $\bar{X}$	0.58 $\bar{X}$
Carbon tetrachloride.....	1.10C–1.68	0.12 $\bar{X}$ +0.25	0.11 $\bar{X}$ +0.37
Chlorobenzene.....	0.98C+2.28	0.16 $\bar{X}$ –0.09	0.26 $\bar{X}$ –1.92
Chloroethane.....	1.18C+0.81	0.14 $\bar{X}$ +2.78	0.29 $\bar{X}$ +1.75
2-Chloroethylvinyl ether.....	1.00C	0.62 $\bar{X}$	0.84 $\bar{X}$
Chloroform.....	0.93C+0.33	0.16 $\bar{X}$ +0.22	0.18 $\bar{X}$ +0.16
Chloromethane.....	1.03C–1.81	0.37 $\bar{X}$ +2.14	0.58 $\bar{X}$ +0.43
Dibromochloromethane.....	1.01C–0.03	0.17 $\bar{X}$ –0.18	0.17 $\bar{X}$ +0.49
1,2-Dichlorobenzene.....	0.94C+4.47	0.22 $\bar{X}$ –1.45	0.30 $\bar{X}$ –1.20
1,3-Dichlorobenzene.....	1.06C+1.68	0.14 $\bar{X}$ –0.48	0.18 $\bar{X}$ –0.82
1,4-Dichlorobenzene.....	0.94C+4.47	0.22 $\bar{X}$ –1.45	0.30 $\bar{X}$ –1.20
1,1-Dichloroethane.....	1.05C+0.36	0.13 $\bar{X}$ –0.05	0.16 $\bar{X}$ +0.47
1,2-Dichloroethane.....	1.02C+0.45	0.17 $\bar{X}$ –0.32	0.21 $\bar{X}$ –0.38
1,1-Dichloroethene.....	1.12C+0.61	0.17 $\bar{X}$ +1.06	0.43 $\bar{X}$ –0.22
trans-1,2-Dichloroethene.....	1.05C+0.03	0.14 $\bar{X}$ +0.09	0.19 $\bar{X}$ +0.17
1,2-Dichloropropane.....	1.00C	0.33 $\bar{X}$	0.45 $\bar{X}$
cis-1,3-Dichloropropene.....	1.00C	0.38 $\bar{X}$	0.52 $\bar{X}$
trans-1,3-Dichloropropene.....	1.00C	0.25 $\bar{X}$	0.34 $\bar{X}$
Ethyl benzene.....	0.98C+2.48	0.14 $\bar{X}$ +1.00	0.26 $\bar{X}$ –1.72
Methylene chloride.....	0.87C+1.88	0.15 $\bar{X}$ +1.07	0.32 $\bar{X}$ +4.00
1,1,2,2-Tetrachloroethane.....	0.93C+1.76	0.16 $\bar{X}$ +0.69	0.20 $\bar{X}$ +0.41

TABLE 6.—METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 624—Continued

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single analyst precision, s_y ($\mu\text{g/L}$)	Overall precision, S ($\mu\text{g/L}$)
Tetrachloroethene	$1.06C + 0.80$	$0.13\bar{X} - 0.18$	$0.16\bar{X} - 0.45$
Toluene	$0.98C + 2.03$	$0.15\bar{X} - 0.71$	$0.22\bar{X} - 1.71$
1,1,1-Trichloroethane	$1.06C + 0.73$	$0.12\bar{X} - 0.15$	$0.21\bar{X} - 0.39$
1,1,2-Trichloroethane	$0.95 + 1.71$	$0.14\bar{X} + 0.02$	$0.18\bar{X} + 0.00$
Trichloroethene	$1.04C + 2.27$	$0.13\bar{X} + 0.36$	$0.12\bar{X} + 0.59$
Trichlorofluoromethane	$0.99C + 0.39$	$0.33\bar{X} - 1.48$	$0.34\bar{X} - 0.39$
Vinyl chloride	1.00C	$0.48\bar{X}$	$0.65\bar{X}$

$\bar{X}$ = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

S_y = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

* Estimates based upon the performance in a single laboratory.¹²

* Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

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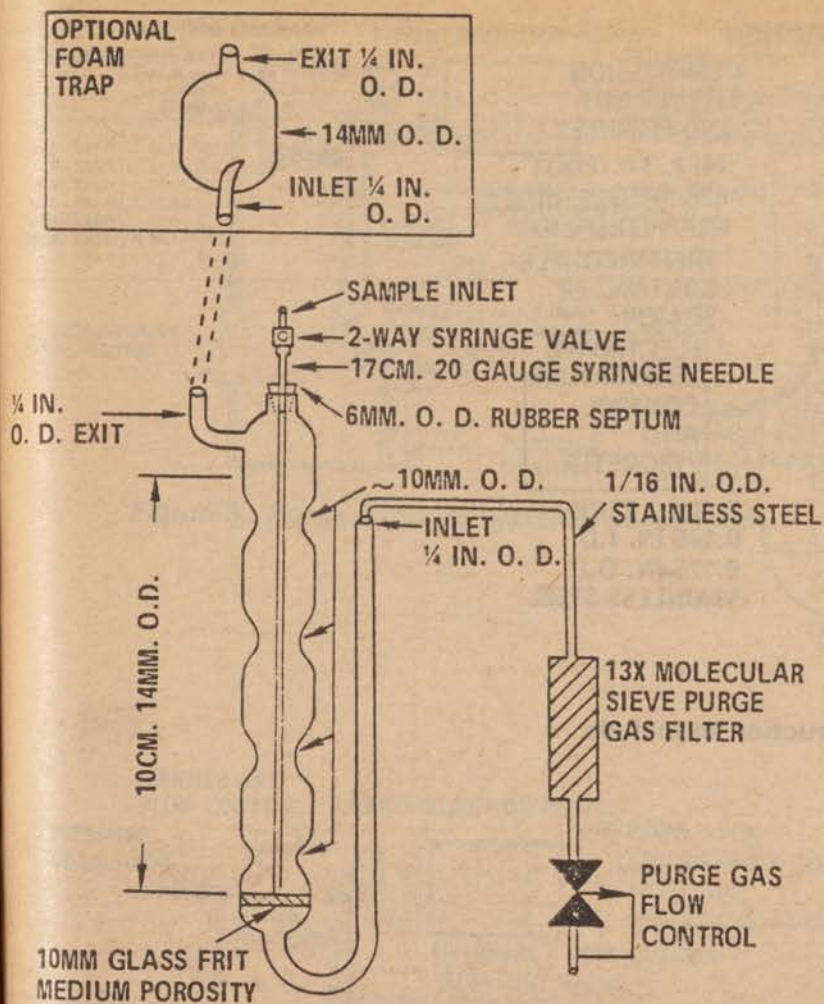


Figure 1. Purging device.

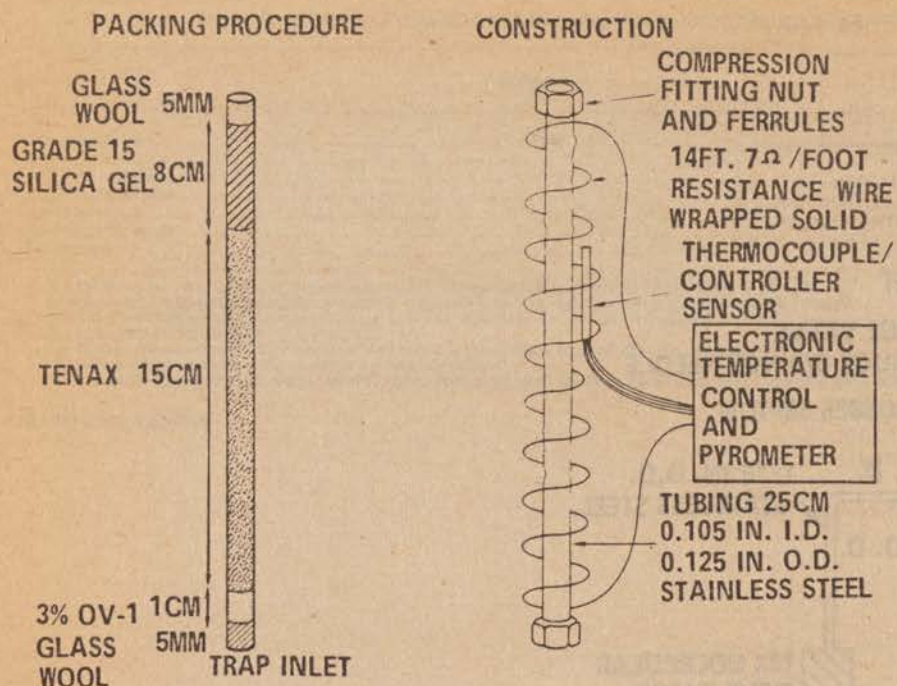


Figure 2. Trap packings and construction to include desorb capability.

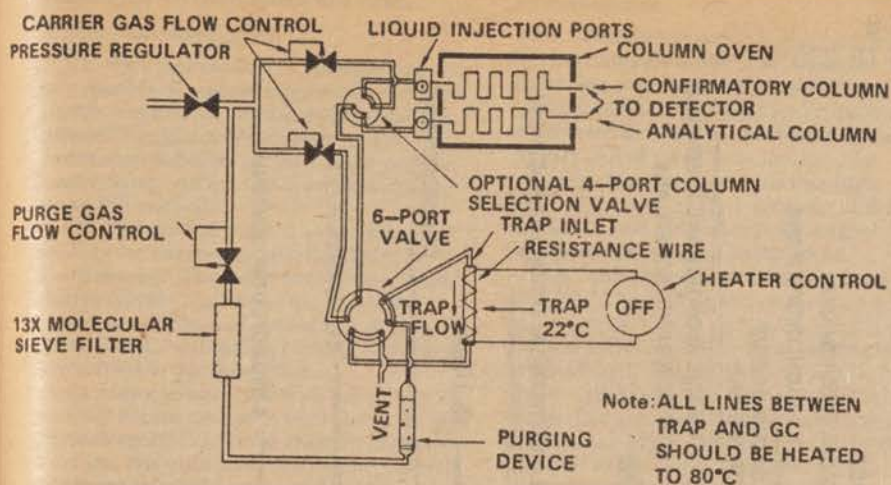


Figure 3. Purge and trap system - purge mode.

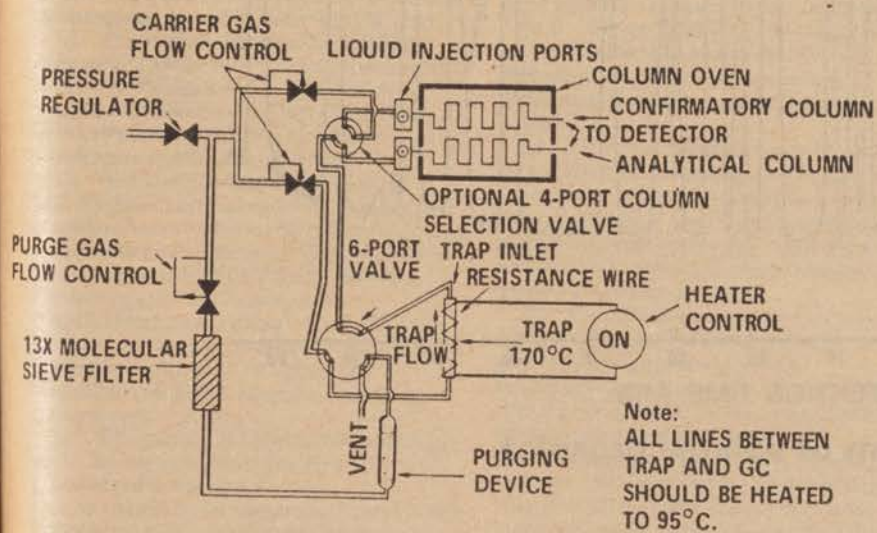


Figure 4. Purge and trap system - desorb mode.

COLUMN: 1% SP-1000 ON CARBOPACK-B
PROGRAM: 45°C FOR 3 MIN, 8°C/MIN TO 220°C
DETECTOR: MASS SPECTROMETER

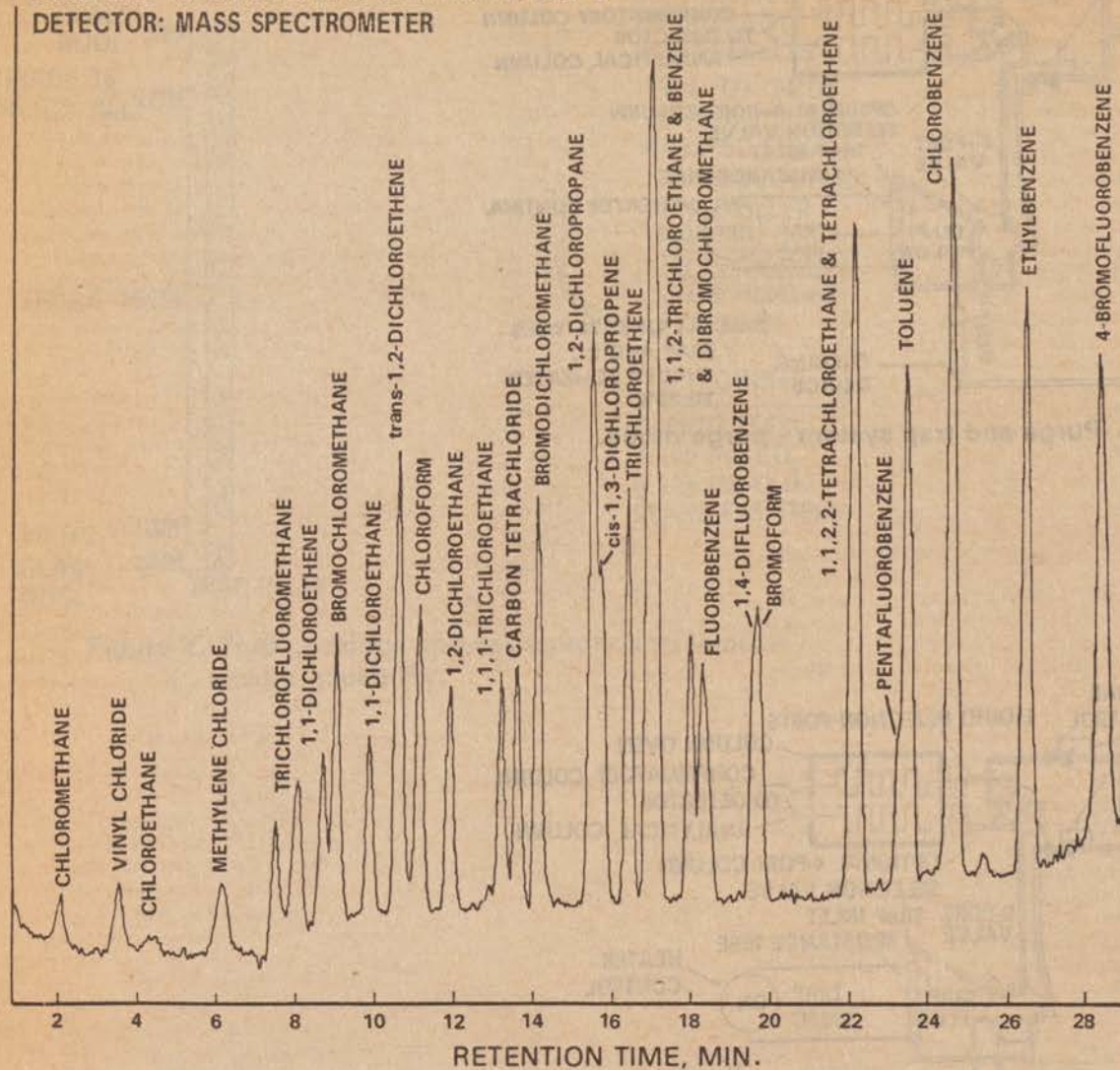


Figure 5. Gas chromatogram of volatile organics.

Method 625—Base/Neutrals and Acids**1. Scope and Application**

1.1 This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and are amenable to gas chromatography. The parameters listed in Tables 1 and 2 may be qualitatively and quantitatively determined using this method.

1.2 The method may be extended to include the parameters listed in Table 3. Benzidine can be subject to oxidative losses during solvent concentration. Under the alkaline conditions of the extraction step, α -BHC, γ -BHC, endosulfan I and II, and endrin are subject to decomposition. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. The preferred method for each of these parameters is listed in Table 3.

1.3 This is a gas chromatographic/mass spectrometry (GC/MS) method applicable to the determination of the compounds listed in Tables 1, 2, and 3 in municipal and industrial discharges as provided under 40 CFR 136.1.

1.4 The method detection limit (MDL, defined in Section 16.1)¹ for each parameter is listed in Tables 4 and 5. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 Any modification to this method, beyond those expressly permitted, shall be considered as a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5. Depending upon the nature of the modification and the extent of intended use, the applicant may be required to demonstrate that the modifications will produce equivalent results when applied to relevant wastewaters.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of a gas chromatograph/mass spectrometer and in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

2. Summary of Method

2.1 A measured volume of sample, approximately 1-L, is serially extracted with methylene chloride at a pH greater than 11 and again at a pH less than 2 using a separatory funnel or a continuous extractor. The methylene chloride extract is dried, concentrated to a volume of 1 mL, and analyzed by GC/MS. Qualitative identification of the parameters in the extract is performed using the retention time and the relative abundance of three characteristic masses (m/z). Quantitative analysis is performed using either external or internal standard techniques with a single characteristic m/z .

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the total ion current profiles. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.3.

3.1.1 Glassware must be scrupulously cleaned.² Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Solvent rinsing should be followed by detergent washing with hot water, and rinses with tap water and distilled water. The glassware should then be drained dry, and heated in a muffle furnace at 400 °C for 15 to 30 min. Some thermally stable materials, such as PCBs, may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Thorough rinsing with such solvents usually eliminates PCB interference. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled.

3.3 The base-neutral extraction may cause significantly reduced recovery of phenol, 2-methylphenol, and 2,4-dimethylphenol. The analyst must recognize that results obtained under these conditions are minimum concentrations.

3.4 The packed gas chromatographic columns recommended for the basic fraction may not exhibit sufficient resolution for certain isomeric pairs including the following: anthracene and phenanthrene; chrysene and benzo(a)anthracene; and benzo(b)fluoranthene and benzo(k)fluoranthene. The gas chromatographic retention time and mass spectra for these pairs of compounds are not sufficiently different to make an unambiguous identification. Alternative techniques should be used to identify and quantify these specific compounds, such as Method 610.

3.5 In samples that contain an inordinate number of interferences, the use of chemical ionization (CI) mass spectrometry may make identification easier. Tables 6 and 7 give characteristic CI ions for most of the compounds covered by this method. The use of CI mass spectrometry to support electron ionization (EI) mass spectrometry is encouraged but not required.

4. Safety.

4.1 The toxicity or carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified ^{3,4} for the information of the analyst.

4.2 The following parameters covered by this method have been tentatively classified as known or suspected, human or mammalian carcinogens: benzo(a)anthracene, benzidine, 3,3'-dichlorobenzidine, benzo(a)pyrene, α -BHC, β -BHC, δ -BHC, γ -BHC, dibenzo(a,h)anthracene, N-nitrosodimethylamine, 4,4'-DDT, and polychlorinated biphenyls (PCBs). Primary standards of these toxic compounds should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle—1-L or 1-gt, amber glass, fitted with a screw cap lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The bottle and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional)—The sampler must incorporate glass sample containers for the collection of a minimum of 250 mL of sample. Sample containers must be kept refrigerated at 4 °C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing should be thoroughly rinsed with methanol, followed by repeated rinsings with distilled water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.):

5.2.1 Separatory funnel—2-L, with Teflon stopcock.

5.2.2 Drying column—Chromatographic column, 19 mm ID, with coarse frit filter disc.

5.2.3 Concentrator tube, Kuderna-Danish—10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish—500-mL (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish—Three all macro (Kontes K-503000-0121 or equivalent).

5.2.6 Snyder column, Kuderna-Danish—Two-ball macro (Kontes K-569001-0219 or equivalent).

5.2.7 Vials—10 to 15-mL, amber glass, with Teflon-lined screw cap.

5.2.8 Continuous liquid—liquid extractor—Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication. (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, N.J., P/N 6841-10 or equivalent.)

5.3 Boiling chips—Approximately 10/40 mesh. Heat to 400 °C for 30 min of Soxhlet extract with methylene chloride.

5.4 Water bath—Heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$). The bath should be used in a hood.

5.5 Balance—Analytical, capable of accurately weighing 0.0001 g.

5.6 GC/MS system:

5.6.1 Gas Chromatograph—An analytical system complete with a temperature programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases. The injection port must be designed for on-column injection when using packed columns and for splitless injection when using capillary columns.

5.6.2 Column for base/neutral—1.8 m long x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are provided in Section 13.1.

5.6.3 Column for acids—1.8 m long x 2 mm ID glass, packed with 1% SP-1240DA on Supelcoport (100/120 mesh) or equivalent. This column was used to develop the method performance statements in Section 16. Guidelines for the use of alternate column packings are given in Section 13.1.

5.6.4 Mass spectrometer—Capable of scanning from 35 to 450 amu every 7 s or less, utilizing a 70 V (nominal) electron energy in the electron impact ionization mode, and producing a mass spectrum which meets all the criteria in Table 9 when 50 ng of decafluorotriphenyl phosphine (DFTPP; bis(perfluorophenyl) phenyl phosphine) is injected through the GC inlet.

5.6.5 GC/MS interface—Any GC to MS interface that gives acceptable calibration points at 50 ng per injection for each of the parameters of interest and achieves all acceptable performance criteria (Section 12) may be used. GC to MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

5.6.6 Data system—A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for specific

m/z and plotting such m/z abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

6. Reagents

6.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

6.2 Sodium hydroxide solution (10 N)—Dissolve 40 g of NaOH (ACS) in reagent water and dilute to 100 mL.

6.3 Sodium thiosulfate—(ACS) Granular.

6.4 Sulfuric acid (1+1)—Slowly, add 50 mL of H_2SO_4 (ACS, sp. gr. 1.84) to 50 mL of reagent water.

6.5 Acetone, methanol, methylene chloride—Pesticide quality or equivalent.

6.6 Sodium sulfate—(ACS) Granular, anhydrous. Purify by heating at 400 °C for 4 h in a shallow tray.

6.7 Stock standard solutions (1.00 $\mu\text{g}/\mu\text{L}$)—standard solutions can be prepared from pure standard materials or purchased as certified solutions.

6.7.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4 °C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.7.3 Stock standard solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

6.8 Surrogate standard spiking solution—Select a minimum of three surrogate compounds from Table 8. Prepare a surrogate standard spiking solution containing each selected surrogate compound at a concentration of 100 $\mu\text{g}/\text{mL}$ in acetone. Addition of 1.00 mL of this solution to 1000 mL of sample is equivalent to a concentration of 100 $\mu\text{g}/\text{L}$ of each surrogate standard. Store the spiking solution at 4 °C in Teflon-sealed glass container. The solution should be checked frequently for stability. The solution must be replaced after six months, or sooner if comparison with quality control check standards indicates a problem.

6.9 DFTPP standard—Prepare a 25 $\mu\text{g}/\text{mL}$ solution of DFTPP in acetone.

6.10 Quality control check sample concentrate—See Section 8.2.1.

7. Calibration

7.1 Establish gas chromatographic operating parameters equivalent to those indicated in Tables 4 or 5.

7.2 Internal standard calibration procedure—To use this approach, the analyst must select three or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Some recommended internal standards are listed in Table 8. Use the base peak m/z as the primary m/z for quantification of the standards. If interferences are noted, use one of the next two most intense masses for quantification.

7.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding appropriate volumes of one or more stock standards to a volumetric flask. To each calibration standard or standard mixture, add a known constant amount of one or more internal standards, and dilute to volume with acetone. One of the calibration standards should be at a concentration near, but above, the MDL and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.2.2 Using injections of 2 to 5 μL , analyze each calibration standard according to Section 13 and tabulate the area of the primary characteristic m/z (Tables 4 and 5) against concentration for each compound and internal standard. Calculate response factors (RF) for each compound using Equation 1.

Equation 1.

$$\text{RF} = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

where:

A_s = Area of the characteristic m/z for the parameter to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

C_{is} = Concentration of the internal standard ($\mu\text{g}/\text{L}$).

C_s = Concentration of the parameter to be measured ($\mu\text{g}/\text{L}$).

If the RF value over the working range is a constant ($< 35\%$ RSD), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_s/A_{is} , vs. RF.

7.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than $\pm 20\%$, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

8. Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.1.1 The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of advances that are occurring in chromatography, the analyst is permitted certain options (detailed in Sections 10.6 and 13.1) to improve the separations or lower the cost of measurements. Each time such a modification is made to the method, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 Before processing any samples, the analyst must analyze a reagent water blank to demonstrate that interferences from the analytical system and glassware are under control. Each time a set of samples is extracted or reagents are changed, a reagent water blank must be processed as a safeguard against laboratory contamination.

8.1.4 The laboratory must, on an ongoing basis, spike and analyze a minimum of 5% of all samples to monitor and evaluate laboratory data quality. This procedure is described in Section 8.3.

8.1.5 The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.4. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed but may be reduced if spike recoveries from samples (Section 8.3) meet all specified quality control criteria.

8.1.6 The laboratory must maintain performance records to document the quality of data that is generated. This procedure is described in Section 8.5.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 A quality control (QC) check sample concentrate is required containing each parameter of interest at a concentration of 100 µg/mL in acetone. Multiple solutions may be required. PCBs and multicomponent pesticides may be omitted from this test. The QC check sample concentrate must be obtained from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory in Cincinnati, Ohio, if available. If not available from that source, the QC check sample concentrate must be obtained from another external source. If not available from either source above, the QC check sample concentrate must be prepared by the laboratory using stock standards

prepared independently from those used for calibration.

8.2.2 Using a pipet, prepare QC check samples at a concentration of 100 µg/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.2.3 Analyze the well-mixed QC check samples according to the method beginning in Section 10 or 11.

8.2.4 Calculate the average recovery ($\bar{X}$) in µg/L, and the standard deviation of the recovery (s) in µg/L, for each parameter using the four results.

8.2.5 For each parameter compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all parameters of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, the system performance is unacceptable for that parameter.

Note.—The large number of parameters in Table 6 present a substantial probability that one or more will fail at least one of the acceptance criteria when all parameters are analyzed.

8.2.6 When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.2.6.1 or 8.2.6.2.

8.2.6.1 Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with Section 8.2.2.

8.2.6.2 Beginning with Section 8.2.2, repeat the test only for those parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.2.2.

8.3 The laboratory must, on an ongoing basis, spike at least 5% of the samples from each sample site being monitored to assess accuracy. For laboratories analyzing 1 to 20 samples per month, at least one spiked sample per month is required.

8.3.1 The concentration of the spike in the sample should be determined as follows:

8.3.1.1 If, as in compliance monitoring, the concentration of a specific parameter in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.2 If the concentration of a specific parameter in the sample is not being checked against a limit specific to that parameter, the spike should be at 100 µg/L or 1 to 5 times higher than the background concentration determined in Section 8.3.2, whichever concentration would be larger.

8.3.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 µg/L.

8.3.2 Analyze one sample aliquot to determine the background concentration (B) of each parameter. If necessary, prepare a new QC check sample concentrate (Section 8.2.1) appropriate for the background concentrations in the sample. Spike a second sample aliquot with 1.0 mL of the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of each parameter. Calculate each percent recovery (P) as $100(A-B)/T$, where T is the known true value of the spike.

8.3.3 Compare the percent recovery (P) for each parameter with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1.⁷ If spiking was performed at a concentration lower than 100 µg/L, the analyst must use either the QC acceptance criteria in Table 6, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of a parameter: (1) calculate accuracy ($\bar{X}$) using the equation in Table 7, substituting the spike concentration (T) for C ; (2) calculate overall precision (S') using the equation in Table 7, substituting $\bar{X}$ for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100 \bar{X}/T) \pm 2.44(100 S'/T)^{1/2}$.

8.3.4 If any individual P falls outside the designated range for recovery, that parameter has failed the acceptance criteria. A check standard containing each parameter that failed the criteria must be analyzed as described in Section 8.4.

8.4 If any parameter fails the acceptance criteria for recovery in Section 8.3, a QC check standard containing each parameter that failed must be prepared and analyzed.

Note.—The frequency for the required analysis of a QC check standard will depend upon the number of parameters being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of single-component parameters in Table 6 must be measured in the sample in Section 8.3, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spike sample.

8.4.1 Prepare the QC check standard by adding 1.0 mL of QC check sample concentrate (Sections 8.2.1 or 8.3.2) to 1 L of reagent water. The QC check standard needs only to contain the parameters that failed criteria in the test in Section 8.3.

8.4.2 Analyze the QC check standard to determine the concentration measured (A) of each parameter. Calculate each percent recovery (P_s) as $100(A/T)\%$, where T is the true value of the standard concentration.

8.4.3 Compare the percent recovery (P_s) for each parameter with the corresponding QC acceptance criteria found in Table 6. Only parameters that failed the test in Section 8.3 need to be compared with these criteria. If the recovery of any such parameter falls outside the designated range, the

laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.5 As part of the QC program for the laboratory, method accuracy for wastewater samples must be assessed and records must be maintained. After the analysis of five spiked wastewater samples as in Section 8.3, calculate the average percent recovery ($\bar{P}$) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent interval from $\bar{P} - 2s_p$ to $\bar{P} + 2s_p$. If $\bar{P} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each parameter on a regular basis (e.g. after each five to ten new accuracy measurements).

8.6 As a quality control check, the laboratory must spike all samples with the surrogate standard spiking solution as described in Section 10.2, and calculate the percent recovery of each surrogate compound.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon tubing and other potential sources of contamination.

9.2 All sampling must be iced or refrigerated at 4 °C from the time of collection until extraction. Fill the sample bottles and, if residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample and mix well. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine.⁹ Field test kits are available for this purpose.

9.3 All samples must be extracted within 7 days of collection and completely analyzed within 40 days of extraction.

10. Separatory Funnel Extraction

10.1 Samples are usually extracted using separatory funnel techniques. If emulsions will prevent achieving acceptable solvent recovery with separatory funnel extractions, continuous extraction (Section 11) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When sample volumes of 2 L are to be extracted, use 250, 100, and 100-mL volumes of methylene chloride for the serial

extraction of the base/neutrals and 200, 100, and 100-mL volumes of methylene chloride for the acids.

10.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-L separatory funnel. Pipet 1.00 mL of the surrogate standard spiking solution into the separatory funnel and mix well. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution.

10.3 Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask. If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Section 11.3.

10.4 Add a second 60-mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract as the base/neutral fraction.

10.5 Adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Serially extract the acidified aqueous phase three times with 60-mL aliquots of methylene chloride. Collect and combine the extracts in a 250-mL Erlenmeyer flask and label the combined extracts as the acid fraction.

10.6 For each fraction, assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

10.7 For each fraction, pour the combined extract through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as

required to complete the concentration in 15 to 20 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.9 Add another one or two clean boiling chips to the concentrator tube for each fraction and attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60 to 65 °C) so that the concentrator tube is partially immersed in hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches about 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of acetone or methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the extracts will be stored longer than two days, they should be transferred to Teflon-sealed screw-cap vials and labeled base/neutral or acid fraction as appropriate.

10.10 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11. Continuous Extraction

11.1 When experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel in Section 10.3, a continuous extractor should be used.

11.2 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Check the pH of the sample with wide-range pH paper and adjust to pH > 11 with sodium hydroxide solution. Transfer the sample to the continuous extractor and using a pipet, add 1.00 mL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 s to rinse the inner surface. Transfer the solvent to the extractor.

11.3 Repeat the sample bottle rinse with an additional 50 to 100-mL portion of methylene chloride and add the rinse to the extractor.

11.4 Add 200 to 500 mL of methylene chloride to the distilling flask, add sufficient reagent water to ensure proper operation, and extract for 24 h. Allow to cool, then detach the distilling flask. Dry, concentrate,

and seal the extract as in Sections 10.6 through 10.9.

11.5 Charge a clean distilling flask with 500 mL of methylene chloride and attach it to the continuous extractor. Carefully, while stirring, adjust the pH of the aqueous phase to less than 2 using sulfuric acid. Extract for 24 h. Dry, concentrate, and seal the extract as in Sections 10.6 through 10.9.

12. Daily GC/MS Performance Tests

12.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see if acceptable performance criteria are achieved for DFTPP.¹⁰ Each day that benzidine is to be determined, the tailing factor criterion described in Section 12.4 must be achieved. Each day that the acids are to be determined, the tailing factor criterion in Section 12.5 must be achieved.

12.2 These performance tests require the following instrumental parameters:

Electron Energy: 70 V (nominal)
Mass Range: 35 to 450 amu
Scan Time: To give at least 5 scans per peak but not to exceed 7 s per scan.

12.3 DFTPP performance test—At the beginning of each day, inject 2 μ L (50 ng) of DFTPP standard solution. Obtain a background-corrected mass spectra of DFTPP and confirm that all the key m/z criteria in Table 9 are achieved. If all the criteria are not achieved, the analyst must retune the mass spectrometer and repeat the test until all criteria are achieved. The performance criteria must be achieved before any samples, blanks, or standards are analyzed. The tailing factor tests in Sections 12.4 and 12.5 may be performed simultaneously with the DFTPP test.

12.4 Column performance test for base/neutrals—At the beginning of each day that the base/neutral fraction is to be analyzed for benzidine, the benzidine tailing factor must be calculated. Inject 100 ng of benzidine either separately or as a part of a standard mixture that may contain DFTPP and calculate the tailing factor. The benzidine tailing factor must be less than 3.0. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

12.5 Column performance test for acids—At the beginning of each day that the acids are to be determined, inject 50 ng of pentachlorophenol either separately or as a part of a standard mix that may contain DFTPP. The tailing factor for pentachlorophenol must be less than 5. Calculation of the tailing factor is illustrated in Figure 13.¹¹ Replace the column packing if the tailing factor criterion cannot be achieved.

13. Gas Chromatography/Mass Spectrometry

13.1 Table 4 summarizes the recommended gas chromatographic operating conditions for the base/neutral fraction. Table 5 summarizes the recommended gas chromatographic operating conditions for the acid fraction. Included in these tables are retention times and MDL that can be achieved under these conditions. Examples of the separations achieved by these columns

are shown in Figures 1 through 12. Other packed or capillary (open-tubular) columns or chromatographic conditions may be used if the requirements of Section 8.2 are met.

13.2 After conducting the GC/MS performance tests in Section 12, calibrate the system daily as described in Section 7.

13.3 If the internal standard calibration procedure is being used, the internal standard must be added to sample extract and mixed thoroughly immediately before injection into the instrument. This procedure minimizes losses due to adsorption, chemical reaction or evaporation.

13.4 Inject 2 to 5 μ L of the sample extract or standard into the GC/MS system using the solvent-flush technique.¹² Smaller (1.0 μ L) volumes may be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μ L.

13.5 If the response for any m/z exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

13.6 Perform all qualitative and quantitative measurements as described in Sections 14 and 15. When the extracts are not being used for analyses, store them refrigerated at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

14. Qualitative Identification

14.1 Obtain EICPs for the primary m/z and the two other masses listed in Tables 4 and 5. See Section 7.3 for masses to be used with internal and surrogate standards. The following criteria must be met to make a qualitative identification:

14.1.1 The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other.

14.1.2 The retention time must fall within ± 30 s of the retention time of the authentic compound.

14.1.3 The relative peak heights of the three characteristic masses in the EICPs must fall within $\pm 20\%$ of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum can be obtained from a standard analyzed in the GC/MS system or from a reference library.

14.2 Structural isomers that have very similar mass spectra and less than 30 s difference in retention time, can be explicitly identified only if the resolution between authentic isomers in a standard mix is acceptable. Acceptable resolution is achieved if the baseline to valley height between the isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

15. Calculations

15.1 When a parameter has been identified, the quantitation of that parameter will be based on the integrated abundance from the EICP of the primary characteristic m/z in Tables 4 and 5. Use the base peak m/z for internal and surrogate standards. If the sample produces an interference for the primary m/z, use a secondary characteristic m/z to quantitate.

Calculate the concentration in the sample using the response factor (RF) determined in Section 7.2.2 and Equation 3.

Equation 3.

$$\text{Concentration } (\mu\text{g/L}) = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Area of the characteristic m/z for the parameter or surrogate standard to be measured.

A_{is} = Area of the characteristic m/z for the internal standard.

I_s = Amount of internal standard added to each extract (μ g).

V_o = Volume of water extracted (L).

15.2 Report results in μ g/L without correction for recovery data. All QC data obtained should be reported with the sample results.

16. Method Performance

16.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.¹ The MDL concentrations listed in Tables 4 and 5 were obtained using reagent water.¹³ The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

16.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5 to 1300 μ g/L.¹⁴ Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 7.

17. Screening Procedure for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

17.1 If the sample must be screened for the presence of 2,3,7,8-TCDD, it is recommended that the reference material not be handled in the laboratory unless extensive safety precautions are employed. It is sufficient to analyze the base/neutral extract by selected ion monitoring (SIM) GC/MS techniques, as follows:

17.1.1 Concentrate the base/neutral extract to a final volume of 0.2 mL.

17.1.2 Adjust the temperature of the base/neutral column (Section 5.6.2) to 220 °C.

17.1.3 Operate the mass spectrometer to acquire data in the SIM mode using the ions at m/z 257, 320 and 322 and a dwell time no greater than 333 milliseconds per mass.

17.1.4 Inject 5 to 7 μ L of the base/neutral extract. Collect SIM data for a total of 10 min.

17.1.5 The possible presence of 2,3,7,8-TCDD is indicated if all three masses exhibit simultaneous peaks at any point in the selected ion current profiles.

17.1.6 For each occurrence where the possible presence of 2,3,7,8-TCDD is indicated, calculate and retain the relative abundances of each of the three masses.

17.2 False positives to this test may be caused by the presence of single or coeluting combinations of compounds whose mass spectra contain all of these masses.

17.3 Conclusive results of the presence and concentration level of 2,3,7,8-TCDD can

be obtained only from a properly equipped laboratory through the use of EPA Method 613 or other approved alternate test procedures.

References

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TABLE 1.—BASE/NEUTRAL EXTRACTABLES

Parameter	STORET No.	CAS No.
Acenaphthene	34205	83-32-9
Acenaphthylene	34200	208-96-8
Anthracene	34220	120-12-7
Aldrin	39330	309-00-2
Benzo(a)anthracene	34526	56-55-3
Benzo(b)fluoranthene	34230	205-99-2
Benzo(k)fluoranthene	34242	207-08-9
Benzo(a)pyrene	34247	50-32-8
Benzo(ghi)perylene	34521	191-24-2
Benzyl butyl phthalate	34292	85-68-7
β -BHC	39338	319-85-7
δ -BHC	34259	319-86-8
Bis(2-chloroethyl)ether	34273	111-44-4
Bis(2-chloroethoxy)methane	34278	111-91-1
Bis(2-ethylhexyl)phthalate	39100	117-81-7
Bis(2-chloroisopropyl)ether	34283	108-60-1
4-Bromophenyl phenyl ether	34636	101-55-3
Chlordane	39350	57-74-8
2-Chloronaphthalene	34581	91-58-7
4-Chlorophenyl phenyl ether	34641	7005-72-3
Chrysene	34320	218-01-9
4,4'-DDD	39310	72-54-8
4,4'-DDE	39320	72-55-9
4,4'-DDT	39300	50-29-3
Dibenz(a,h)anthracene	34556	53-70-3
Di-n-butylphthalate	39110	84-74-2
1,3-Dichlorobenzene	34566	541-73-1
1,2-Dichlorobenzene	34536	95-50-1
1,4-Dichlorobenzene	34571	106-46-7
3,3'-Dichlorobenzidine	34631	91-94-1
Dieldrin	39380	60-57-1
Diethyl phthalate	34336	84-66-2
Dimethyl phthalate	34341	131-11-3
2,4-Dinitrotoluene	34611	121-14-2
2,6-Dinitrotoluene	34626	806-20-2
Di-n-octylphthalate	34596	117-84-0
Endosulfan sulfate	34351	1031-07-8

TABLE 1.—BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	STORET No.	CAS No.
Endrin aldehyde	34366	7421-93-4
Fluoranthene	34376	206-44-0
Fluorene	34381	86-73-7
Heptachlor	39410	76-44-8
Heptachlor epoxide	39420	1024-57-3
Hexachlorobenzene	39700	118-74-1
Hexachlorobutadiene	34391	87-68-3
Hexachloromethane	34396	67-72-1
Indeno(1,2,3-cd)pyrene	34403	183-39-5
Isophorone	34408	78-59-1
Naphthalene	34696	91-20-3
Nitrobenzene	34447	98-95-3
N-Nitrosodi-n-propylamine	34428	621-64-7
PCB-1016	34671	12674-11-2
PCB-1221	39488	11104-28-2
PCB-1232	39492	11141-16-5
PCB-1242	39496	53469-21-9
PCB-1248	39500	12672-29-8
PCB-1254	39504	11097-69-1
PCB-1260	39508	11096-82-5
Phenanthrene	34461	85-01-8
Pyrene	34469	129-00-0
Toxaphene	39400	8001-35-2
1,2,4-Trichlorobenzene	34551	120-82-1

TABLE 2.—ACID EXTRACTABLES

Parameter	STORET No.	CAS No.
4-Chloro-3-methylphenol	34452	59-50-7
2-Chlorophenol	34586	95-57-8
2,4-Dichlorophenol	34601	120-83-2
2,4-Dimethylphenol	34606	105-67-9
2,4-Dinitrophenol	34616	51-28-5
2-Methyl-4,6-dinitrophenol	34657	534-52-1
2-Nitrophenol	34591	88-75-5
4-Nitrophenol	34648	100-02-7
Pentachlorophenol	39032	87-86-5
Phenol	34694	108-95-2
2,4,6-Trichlorophenol	34621	88-06-2

TABLE 3.—ADDITIONAL EXTRACTABLE PARAMETERS*

Parameter	STORET No.	CAS No.	Method
Benzidine	39120	92-87-5	605
β -BHC	39337	319-84-6	608
δ -BHC	39340	58-89-8	608
Endosulfan I	34361	959-98-8	608
Endosulfan II	34358	33213-65-9	608
Endrin	39390	72-20-8	608
Hexachlorocyclopentadiene	34386	77-47-4	612
N-Nitrosodimethylamine	34438	62-75-9	607
N-Nitrosodiphenylamine	34433	86-30-6	607

* See Section 1.2.

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit ($\mu\text{g/L}$)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propylamine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	85	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene*	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181

TABLE 4.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR BASE/NEUTRAL EXTRACTABLES—Continued

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
Acenaphthene	17.8	1.9	154	153	152	154	155	163
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	168	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	185	63	182	183	211	223
Diethylphthalate	20.1	1.9	149	177	150	177	223	251
N-Nitrosodiphenylamine*	20.6	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
β-BHC*	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
δ-BHC*	22.4		183	181	109			
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I*	26.4		237	338	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin*	27.9		81	263	82			
Endosulfan II*	28.6		237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine*	28.8	4.4	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde			67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethylamine*			42	74	44			
Chlordane*	19-30		373	375	377			
Toxaphene*	25-34		159	231	233			
PCB 1016*	18-30		224	260	294			
PCB 1221*	15-30	30	190	224	260			
PCB 1232*	15-32		190	224	260			
PCB 1242*	15-32		224	260	294			
PCB 1248*	12-34		294	330	262			
PCB 1254*	22-34	36	294	330	362			
PCB 1260*	23-32		330	362	394			

* See Section 1.2.

* These compounds are mixtures of various isomers. (See figures 2 thru 12.)

Column conditions: Supelcoport (100/120 mesh) coated with 3% SP-2250 packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 50 °C for 4 min, then programmed at 8 °C/min to 270 °C and held for 30 min.

TABLE 5.—CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC MASSES FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/L)	Characteristic masses					
			Electron impact			Chemical ionization		
			Primary	Secondary	Secondary	Methane	Methane	Methane
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.8	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	96	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Column conditions: Supelcoport (100/120 mesh) coated with 1% SP-1240DA packed in a 1.8 m long x 2mm ID glass column with helium carrier gas at 30 mL/min flow rate. Column temperature held isothermal at 70 °C for 2 min then programmed at 8 °C/min to 200 °C.

TABLE 6.—QC ACCEPTANCE CRITERIA—METHOD 625

Parameter	Test conclusion ($\mu\text{g/L}$)	Limits for s ($\mu\text{g/L}$)	Range for $\bar{X}$ ($\mu\text{g/L}$)	Range for P, P _s (Percent)
Acenaphthene	100	27.6	80.1–132.3	47–145
Acenaphthylene	100	40.2	53.5–126.0	33–145
Aldrin	100	39.0	7.2–152.2	D-166
Anthracene	100	32.0	43.4–118.0	27–133
Benzo(a)anthracene	100	27.6	41.8–133.0	33–143
Benzo(b)fluoranthene	100	38.8	42.0–140.4	24–159
Benzo(k)fluoranthene	100	32.3	25.2–145.7	11–162
Benzo(a)pyrene	100	39.0	31.7–148.0	17–163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β -BHC	100	31.5	41.5–130.6	24–149
δ -BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9–126.0	12–158
Bis(2-chloroethoxy)methane	100	34.5	49.2–164.7	33–184
Bis(2-chloroisopropyl)ether	100	46.3	62.8–138.6	36–166
Bis(2-ethylhexyl)phthalate	100	41.1	26.9–136.8	8–158
4-Bromophenyl phenyl ether	100	23.0	64.9–114.4	53–127
2-Chloronaphthalene	100	13.0	64.5–113.5	60–118
4-Chlorophenyl phenyl ether	100	33.4	38.4–144.7	25–158
Chrysene	100	48.3	44.1–139.9	17–166
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2–119.7	4–136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4–111.0	1–118
1,2-Dichlorobenzene	100	30.9	46.6–112.0	32–129
1,3-Dichlorobenzene	100	41.7	16.7–153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3–105.7	20–124
3,3'-Dichlorobenzidine	100	71.4	8.2–212.5	D-262
Dieldrin	100	30.7	44.3–119.3	29–136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5–126.9	39–139
2,6-Dinitrotoluene	100	29.6	68.1–136.7	50–156
Di-n-octylphthalate	100	31.4	18.6–131.8	4–146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-168.8	D-209
Fluoranthene	100	32.8	42.9–121.3	26–137
Fluorene	100	20.7	71.6–108.4	59–121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9–109.4	26–155
Hexachlorobenzene	100	24.9	7.8–141.5	D-152
Hexachlorobutadiene	100	26.3	37.8–102.2	24–116
Hexachloroethane	100	24.5	55.2–100.0	40–113
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6–180.2	21–196
Naphthalene	100	30.1	35.6–119.6	21–133
Nitrobenzene	100	39.3	54.3–157.6	35–180
N-Nitrosodi-n-propylamine	100	55.4	13.6–197.9	D-230
PCB-1260	100	54.2	19.3–121.0	D-164
Phenanthrene	100	20.6	65.2–108.7	54–120
Pyrene	100	25.2	69.6–100.0	52–115
1,2,4-Trichlorobenzene	100	28.1	57.3–129.2	44–142
4-Chloro-3-methylphenol	100	37.2	40.8–127.9	22–147
2-Chlorophenol	100	28.7	36.2–120.4	23–134
2,4-Dichlorophenol	100	26.4	52.5–121.7	39–135
2,4-Dimethylphenol	100	26.1	41.8–109.0	32–119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0–100.0	D-181
2-Nitrophenol	100	35.2	45.0–166.7	29–182
4-Nitrophenol	100	47.2	13.0–106.5	D-132
Pentachlorophenol	100	48.9	38.1–151.8	14–176
Phenol	100	22.6	16.6–100.0	5–112
2,4,6-Trichlorophenol	100	31.7	52.4–129.2	37–144

s = Standard deviation for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4). $\bar{X}$ = Average recovery for four recovery measurements, in $\mu\text{g/L}$ (Section 8.2.4).P, P_s = Percent recovery measured (Section 8.3.2, Section 8.4.2).

D = Detected; result must be greater than zero.

Note: These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625

Parameter	Accuracy, as recovery, $\bar{X}$ ($\mu\text{g/L}$)	Single analyst precision, S_x ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Acenaphthene	0.96C+0.19	0.15 $\bar{X}$ –0.12	0.21 $\bar{X}$ –0.67
Acenaphthylene	0.89C+0.74	0.24 $\bar{X}$ –1.06	0.26 $\bar{X}$ –0.54
Aldrin	0.78C+1.66	0.27 $\bar{X}$ –1.28	0.43 $\bar{X}$ +1.13
Anthracene	0.80C+0.68	0.21 $\bar{X}$ –0.32	0.27 $\bar{X}$ –0.64
Benzo(a)anthracene	0.88C–0.80	0.15 $\bar{X}$ +0.93	0.26 $\bar{X}$ –0.28
Benzo(b)fluoranthene	0.93C–1.80	0.22 $\bar{X}$ +0.43	0.29 $\bar{X}$ +0.96
Benzo(k)fluoranthene	0.87C–1.56	0.19 $\bar{X}$ +1.03	0.35 $\bar{X}$ +0.40
Benzo(a)pyrene	0.90C–0.13	0.22 $\bar{X}$ +0.48	0.32 $\bar{X}$ +1.35
Benzo(ghi)perylene	0.88C–0.86	0.29 $\bar{X}$ +2.40	0.51 $\bar{X}$ –0.44
Benzyl butyl phthalate	0.66C–1.68	0.16 $\bar{X}$ +0.94	0.53 $\bar{X}$ +0.92
β -BHC	0.87C–0.94	0.20 $\bar{X}$ –0.58	0.30 $\bar{X}$ –1.94
δ -BHC	0.29C–1.09	0.34 $\bar{X}$ +0.86	0.93 $\bar{X}$ –0.17
Bis(2-chloroethyl)ether	0.88C–1.54	0.35 $\bar{X}$ –0.99	0.35 $\bar{X}$ +0.10

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION—METHOD 625—Continued

Parameter	Accuracy, as recovery, X' ($\mu\text{g/L}$)	Single analyst precision, S_s ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16 $\bar{X}$ +1.34	0.26 $\bar{X}$ +2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24 $\bar{X}$ +0.28	0.25 $\bar{X}$ +1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26 $\bar{X}$ +0.73	0.36 $\bar{X}$ +0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13 $\bar{X}$ +0.66	0.16 $\bar{X}$ +0.66
2-Chloronaphthalene	0.89C+0.01	0.07 $\bar{X}$ +0.52	0.13 $\bar{X}$ +0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20 $\bar{X}$ -0.94	0.30 $\bar{X}$ -0.46
Chrysene	0.93C-1.00	0.28 $\bar{X}$ +0.13	0.33 $\bar{X}$ -0.09
4,4'-DDD	0.56C-0.40	0.29 $\bar{X}$ -0.32	0.66 $\bar{X}$ -0.96
4,4'-DDE	0.70C-0.54	0.26 $\bar{X}$ -1.17	0.39 $\bar{X}$ -1.04
4,4'-DDT	0.79C-3.28	0.42 $\bar{X}$ +0.19	0.65 $\bar{X}$ -0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30 $\bar{X}$ +8.51	0.59 $\bar{X}$ +0.25
Di-n-butyl phthalate	0.59C+0.71	0.13 $\bar{X}$ +1.16	0.39 $\bar{X}$ +0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20 $\bar{X}$ +0.47	0.24 $\bar{X}$ +0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25 $\bar{X}$ +0.68	0.41 $\bar{X}$ +0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24 $\bar{X}$ +0.23	0.29 $\bar{X}$ +0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28 $\bar{X}$ +7.33	0.47 $\bar{X}$ +3.45
Dieldrin	0.82C-0.16	0.20 $\bar{X}$ -0.16	0.26 $\bar{X}$ -0.07
Diethyl phthalate	0.43C+1.00	0.28 $\bar{X}$ +1.44	0.52 $\bar{X}$ +0.22
Dimethyl phthalate	0.20C+1.03	0.54 $\bar{X}$ +0.19	1.05 $\bar{X}$ -0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12 $\bar{X}$ +1.06	0.21 $\bar{X}$ +1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14 $\bar{X}$ +1.26	0.19 $\bar{X}$ +0.35
Di-n-octylphthalate	0.76C-0.79	0.21 $\bar{X}$ +1.19	0.37 $\bar{X}$ +1.19
Endosulfan sulfate	0.39C+0.41	0.12 $\bar{X}$ +2.47	0.63 $\bar{X}$ -1.03
Endrin aldehyde	0.76C-3.86	0.18 $\bar{X}$ +3.91	0.73 $\bar{X}$ -0.62
Fluoranthene	0.81C+1.10	0.22 $\bar{X}$ -0.73	0.28 $\bar{X}$ -0.60
Fluorene	0.90C-0.00	0.12 $\bar{X}$ +0.26	0.13 $\bar{X}$ +0.61
Heptachlor	0.87C-2.87	0.24 $\bar{X}$ -0.56	0.50 $\bar{X}$ -0.23
Heptachlor epoxide	0.92C-1.87	0.33 $\bar{X}$ -0.46	0.28 $\bar{X}$ +0.64
Hexachlorobenzene	0.74C+0.66	0.18 $\bar{X}$ -0.10	0.43 $\bar{X}$ -0.52
Hexachlorobutadiene	0.71C-1.01	0.19 $\bar{X}$ +0.92	0.26 $\bar{X}$ +0.49
Hexachloroethane	0.73C-0.83	0.17 $\bar{X}$ +0.67	0.17 $\bar{X}$ +0.80
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29 $\bar{X}$ +1.46	0.50 $\bar{X}$ +0.44
Isophorone	1.12C+1.41	0.27 $\bar{X}$ +0.77	0.33 $\bar{X}$ +0.26
Naphthalene	0.76C+1.58	0.21 $\bar{X}$ -0.41	0.30 $\bar{X}$ -0.68
Nitrobenzene	1.09C-3.05	0.19 $\bar{X}$ +0.92	0.27 $\bar{X}$ +0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27 $\bar{X}$ +0.68	0.44 $\bar{X}$ +0.47
PCB-1260	0.81C-10.86	0.35 $\bar{X}$ +3.61	0.43 $\bar{X}$ +1.82
Phenanthrene	0.87C-0.06	0.12 $\bar{X}$ +0.57	0.15 $\bar{X}$ +0.25
Pyrene	0.84C-0.16	0.16 $\bar{X}$ +0.06	0.15 $\bar{X}$ +0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15 $\bar{X}$ +0.85	0.21 $\bar{X}$ +0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23 $\bar{X}$ -0.75	0.29 $\bar{X}$ +1.31
2-Chlorophenol	0.78C+0.29	0.18 $\bar{X}$ +1.46	0.28 $\bar{X}$ +0.97
2,4-Dichlorophenol	0.87C+0.13	0.15 $\bar{X}$ +1.25	0.21 $\bar{X}$ +1.28
2,4-Dimethylphenol	0.71C+4.41	0.16 $\bar{X}$ +1.21	0.22 $\bar{X}$ +1.31
2,4-Dinitrophenol	0.81C-18.04	0.38 $\bar{X}$ +2.36	0.42 $\bar{X}$ +26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10 $\bar{X}$ +42.29	0.26 $\bar{X}$ +23.10
2-Nitrophenol	1.07C-1.15	0.16 $\bar{X}$ +1.94	0.27 $\bar{X}$ +2.60
4-Nitrophenol	0.61C-1.22	0.38 $\bar{X}$ +2.57	0.44 $\bar{X}$ +3.24
Pentachlorophenol	0.93C+1.99	0.24 $\bar{X}$ +3.03	0.30 $\bar{X}$ +4.33
Phenol	0.43C+1.26	0.26 $\bar{X}$ +0.73	0.35 $\bar{X}$ +0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16 $\bar{X}$ +2.22	0.22 $\bar{X}$ +1.81

X' = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

S_s = Expected single analyst standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

$\bar{X}$ = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

TABLE 8.—SUGGESTED INTERNAL AND SURROGATE STANDARDS

Base/neutral fraction	Acid fraction
Aniline- d_5	2-Fluorophenol.
Anthracene- d_{10}	Pentafluorophenol.
Benzo(a)anthracene- d_{12}	Phenol- d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol.
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthylene	
2-Fluoronaphthylene	
Naphthalene- d_8	
Nitrobenzene- d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene- d_{10}	
Pyridine- d_5	

TABLE 9.—DFTPP KEY MASSES AND ABUNDANCE CRITERIA

Mass	m/z Abundance criteria
51	30-60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40-60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17-23 percent of mass 442.

BILLING CODE 6560-50-M

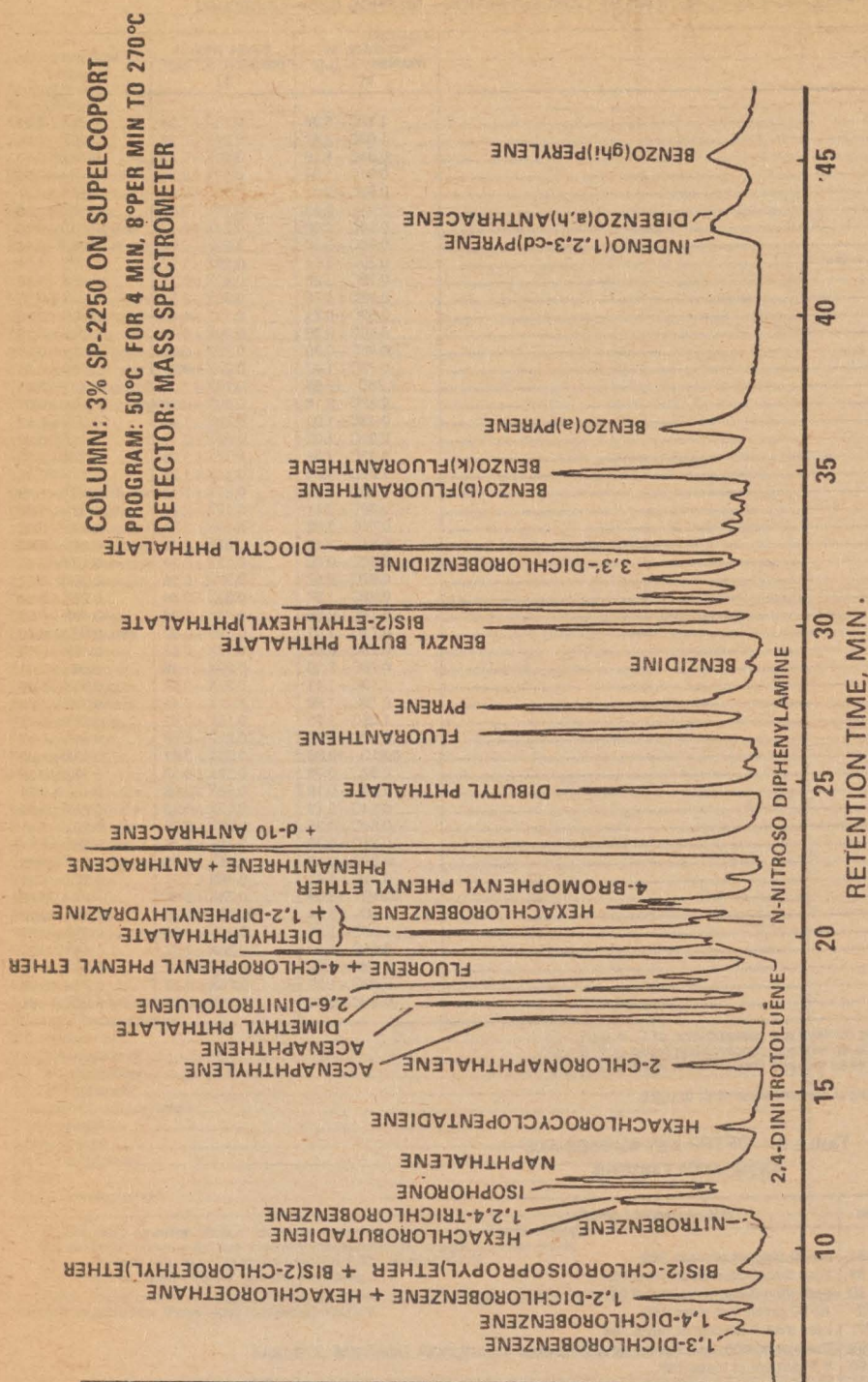


Figure 1. Gas chromatogram of base/neutral fraction.

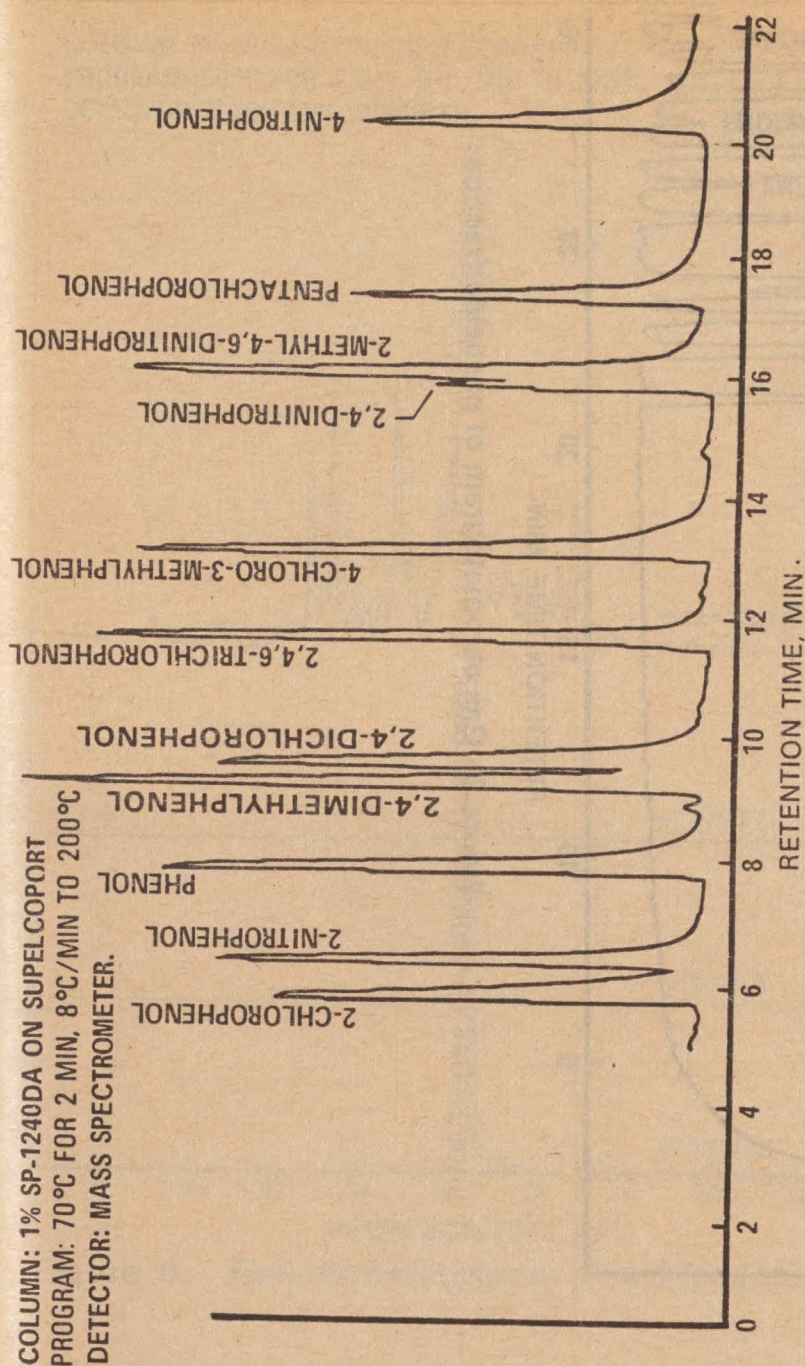


Figure 2. Gas chromatogram of acid fraction.

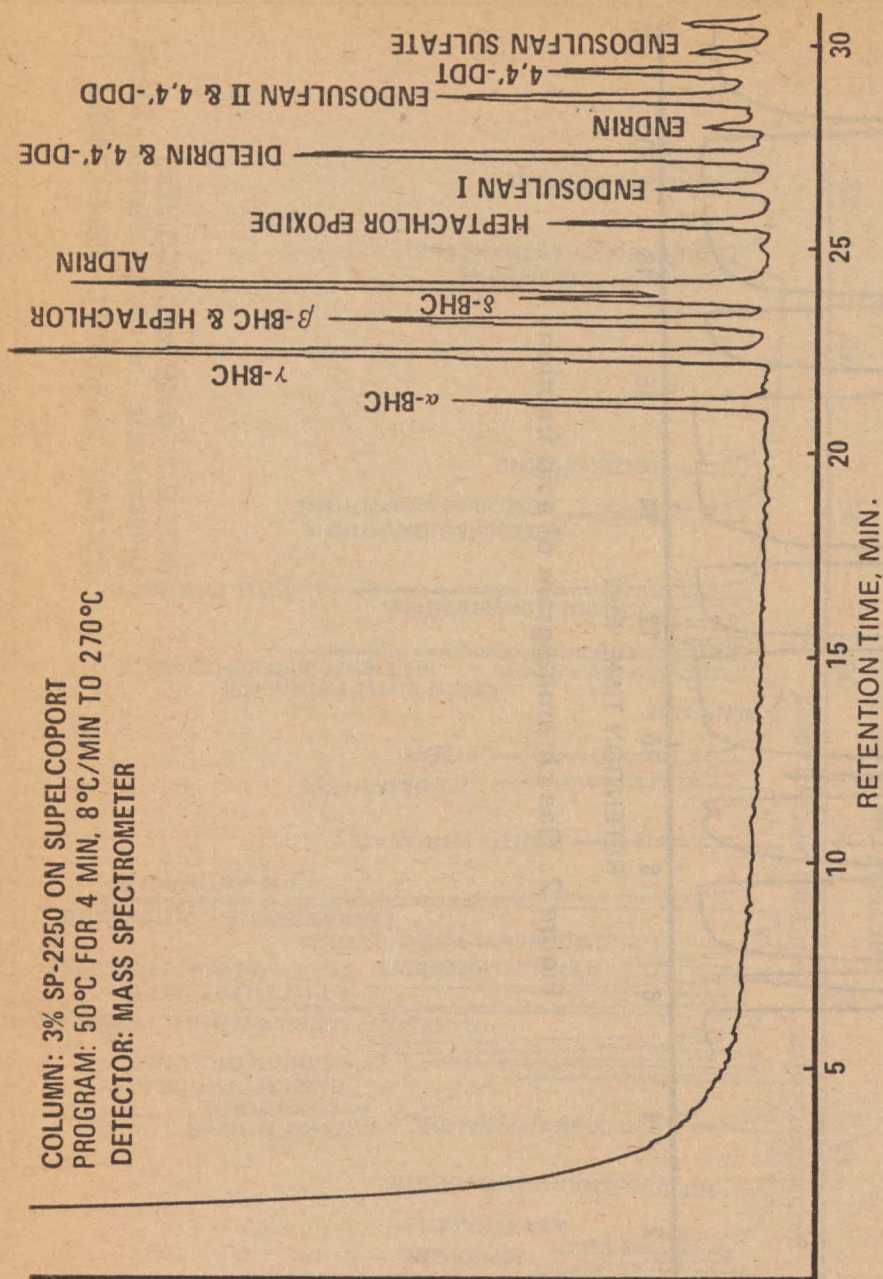


Figure 3. Gas chromatogram of pesticide fraction.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

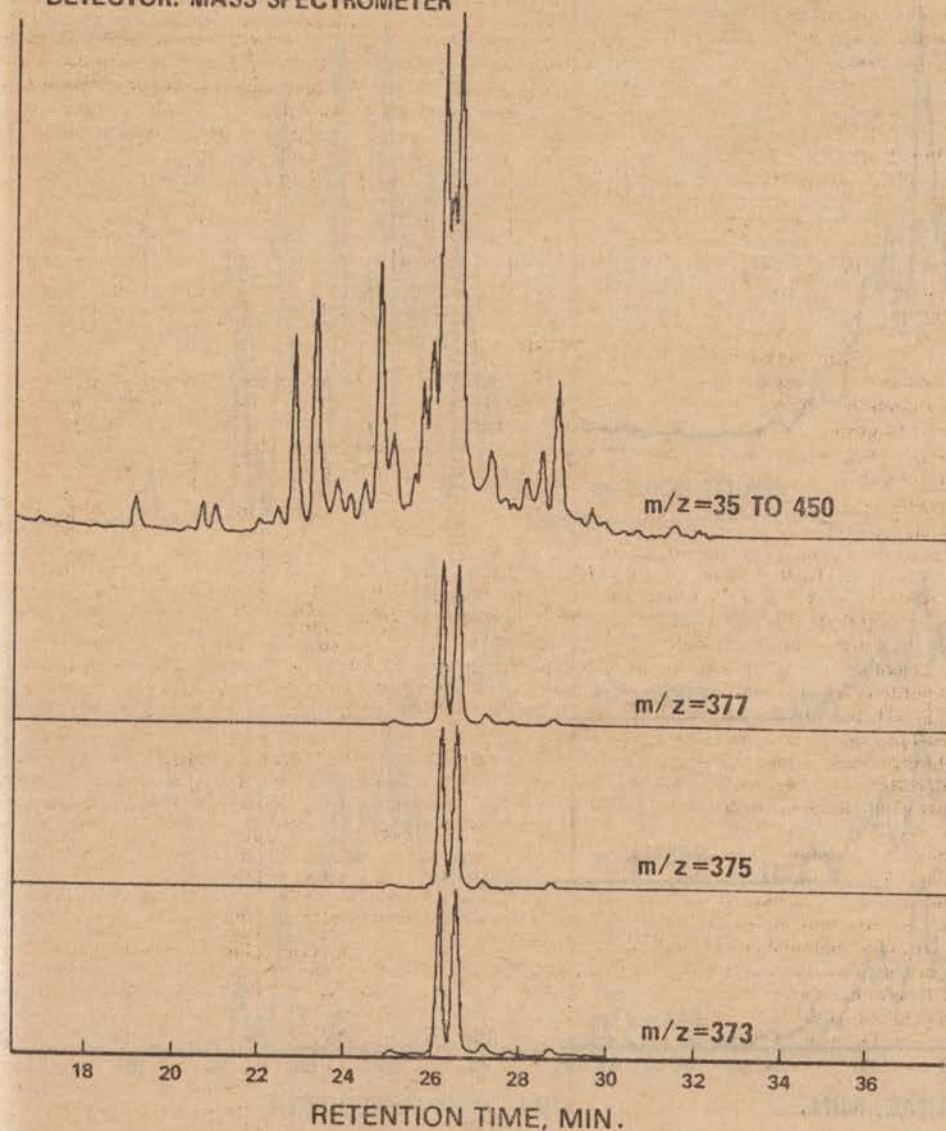


Figure 4. Gas chromatogram of chlordane.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

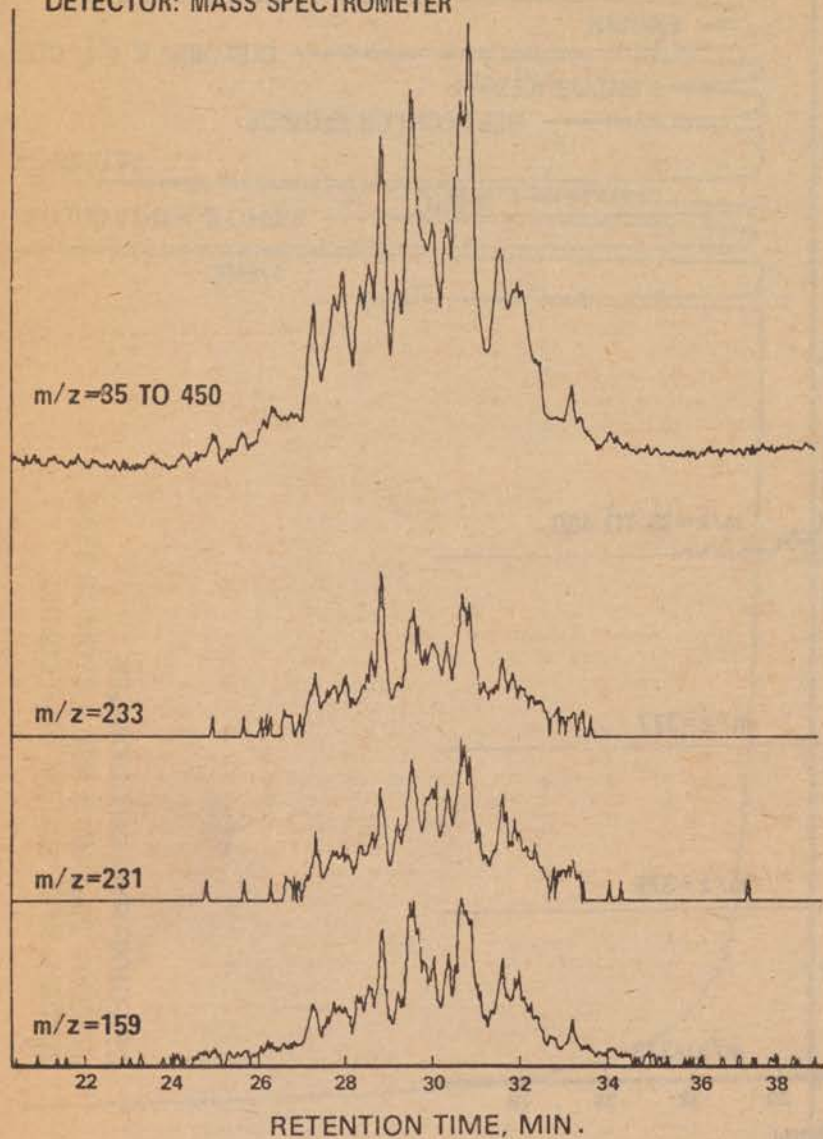


Figure 5. Gas chromatogram of toxaphene.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

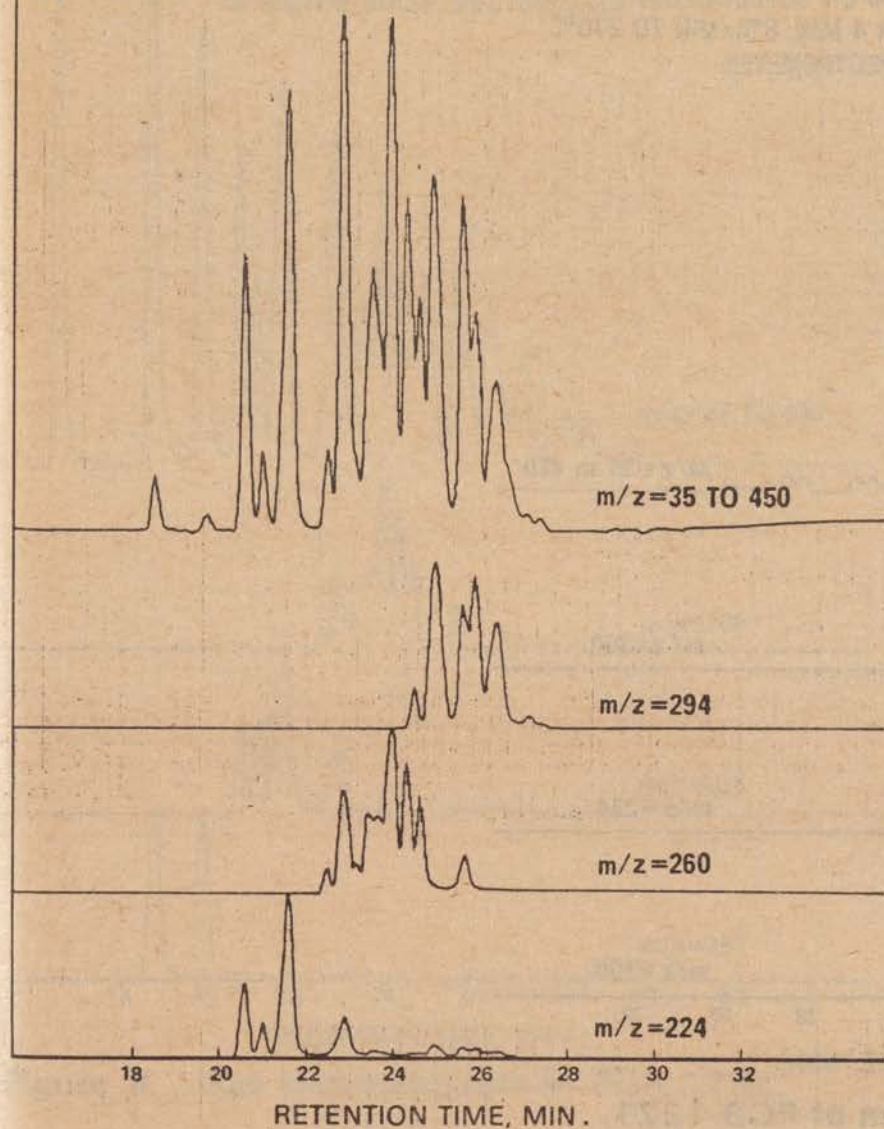


Figure 6. Gas chromatogram of PCB-1016.

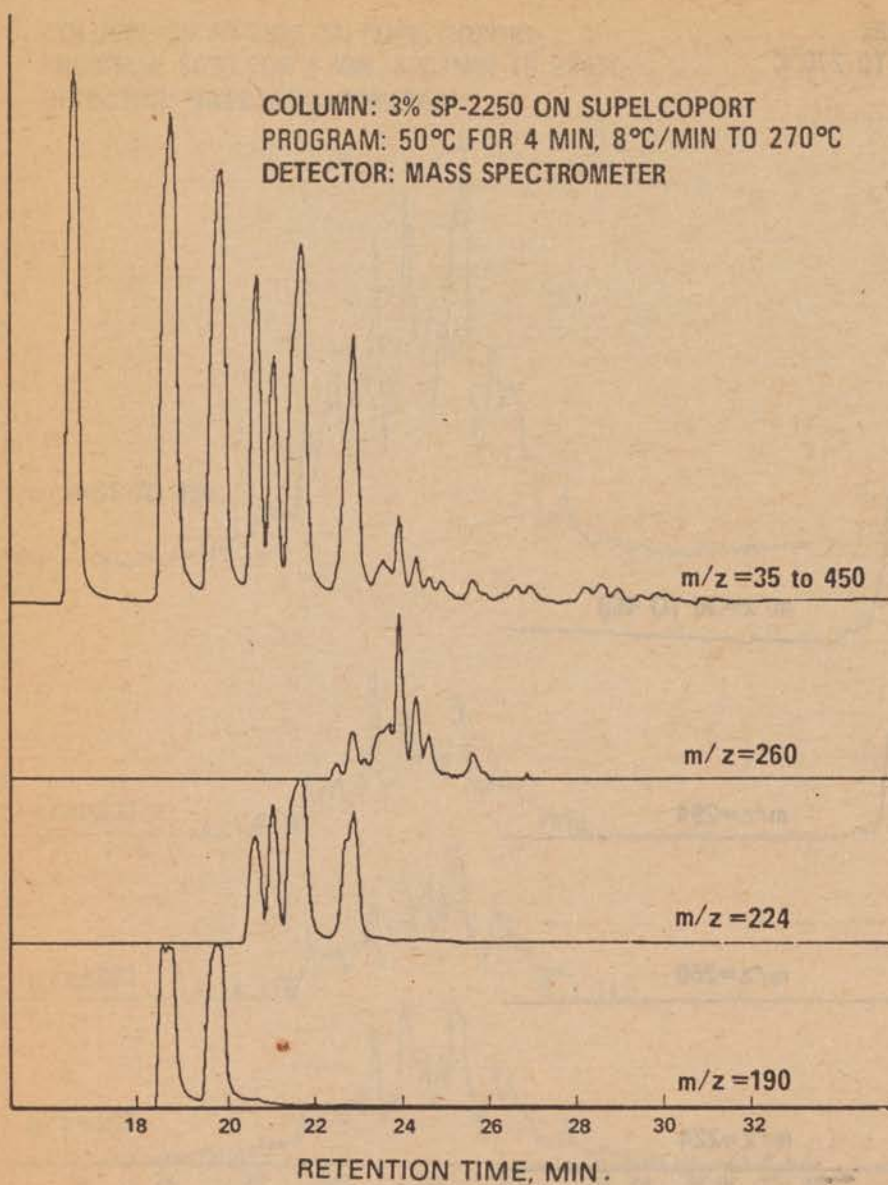


Figure 7. Gas chromatogram of PCB-1221.

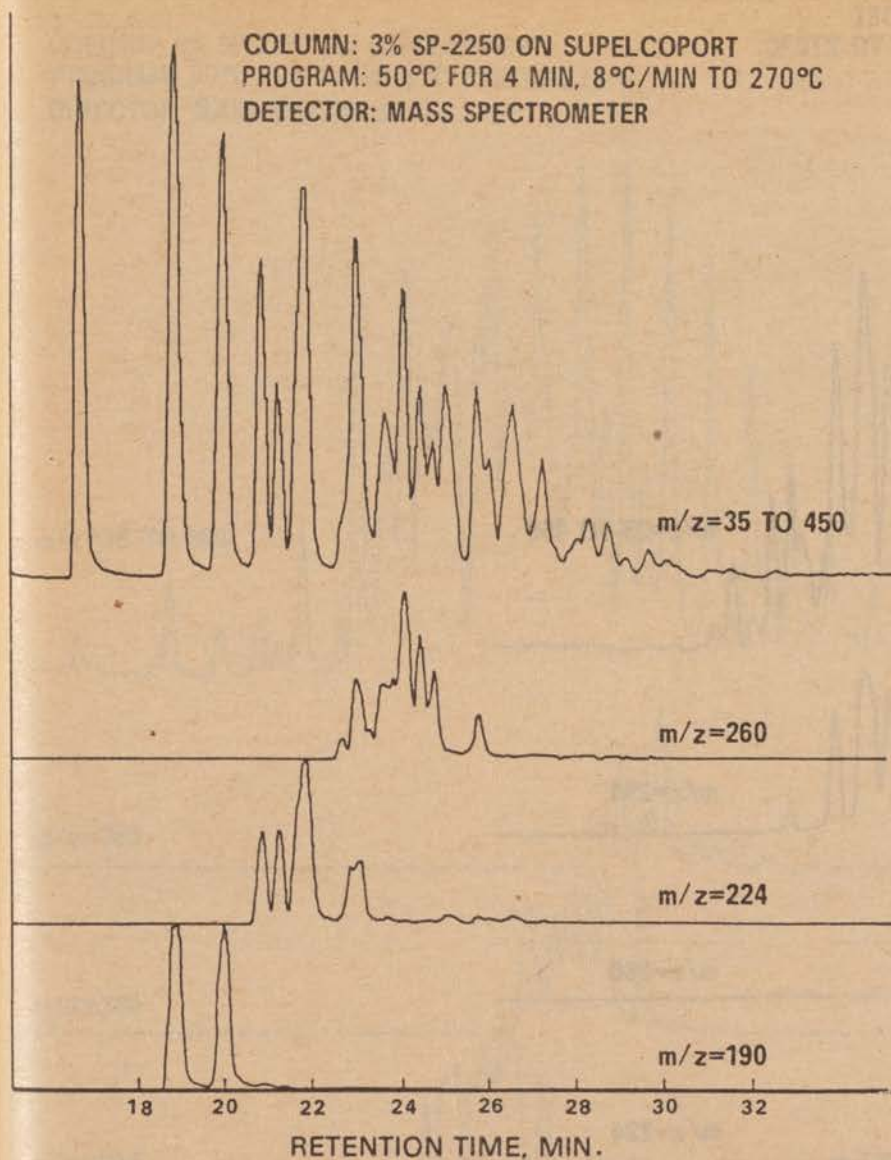


Figure 8. Gas chromatogram of PCB-1232.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

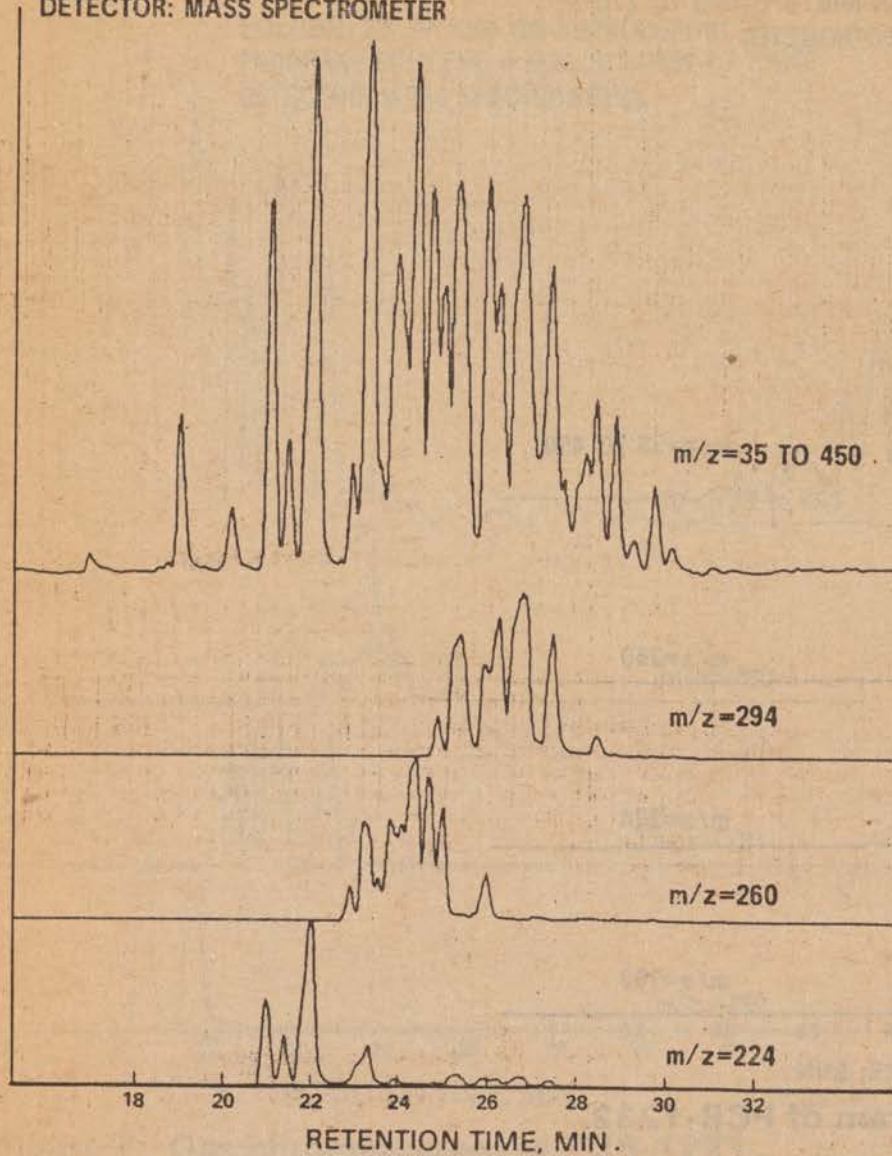


Figure 9. Gas chromatogram of PCB-1242.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

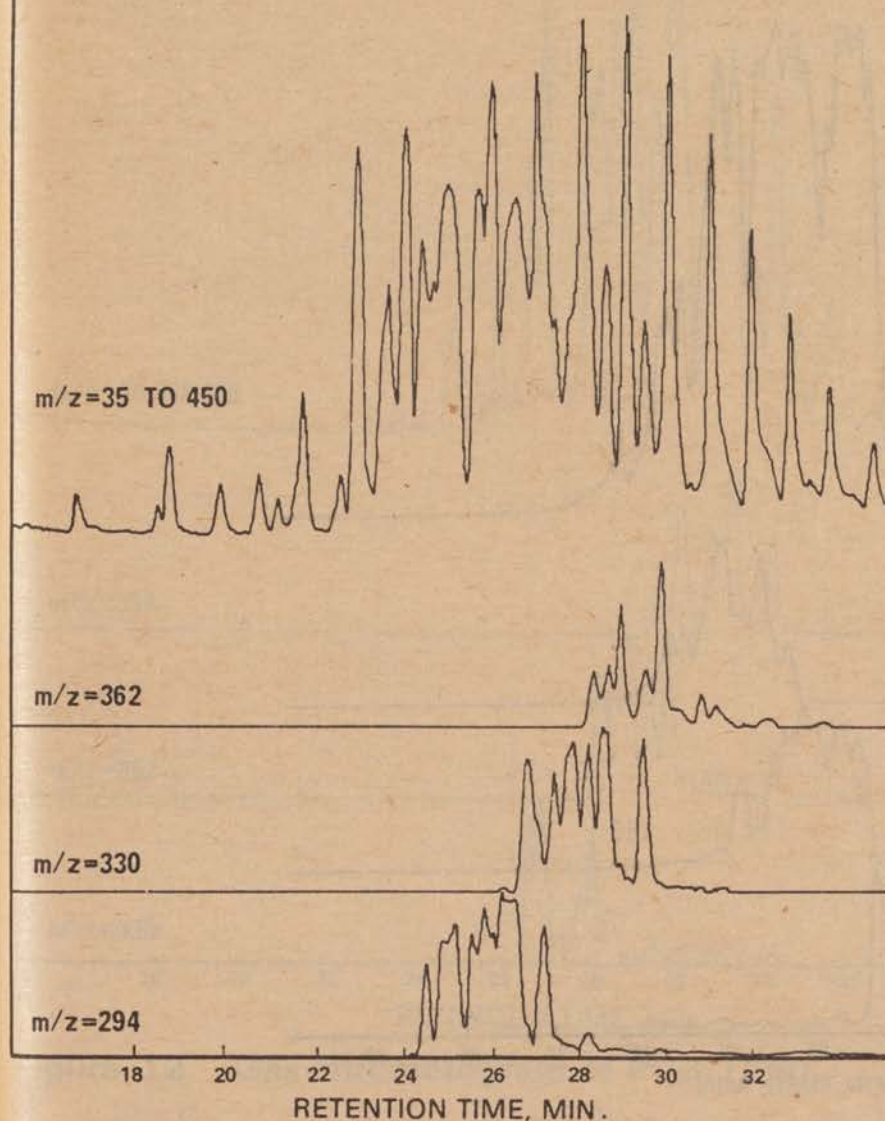


Figure 10. Gas chromatogram of PCB-1248.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

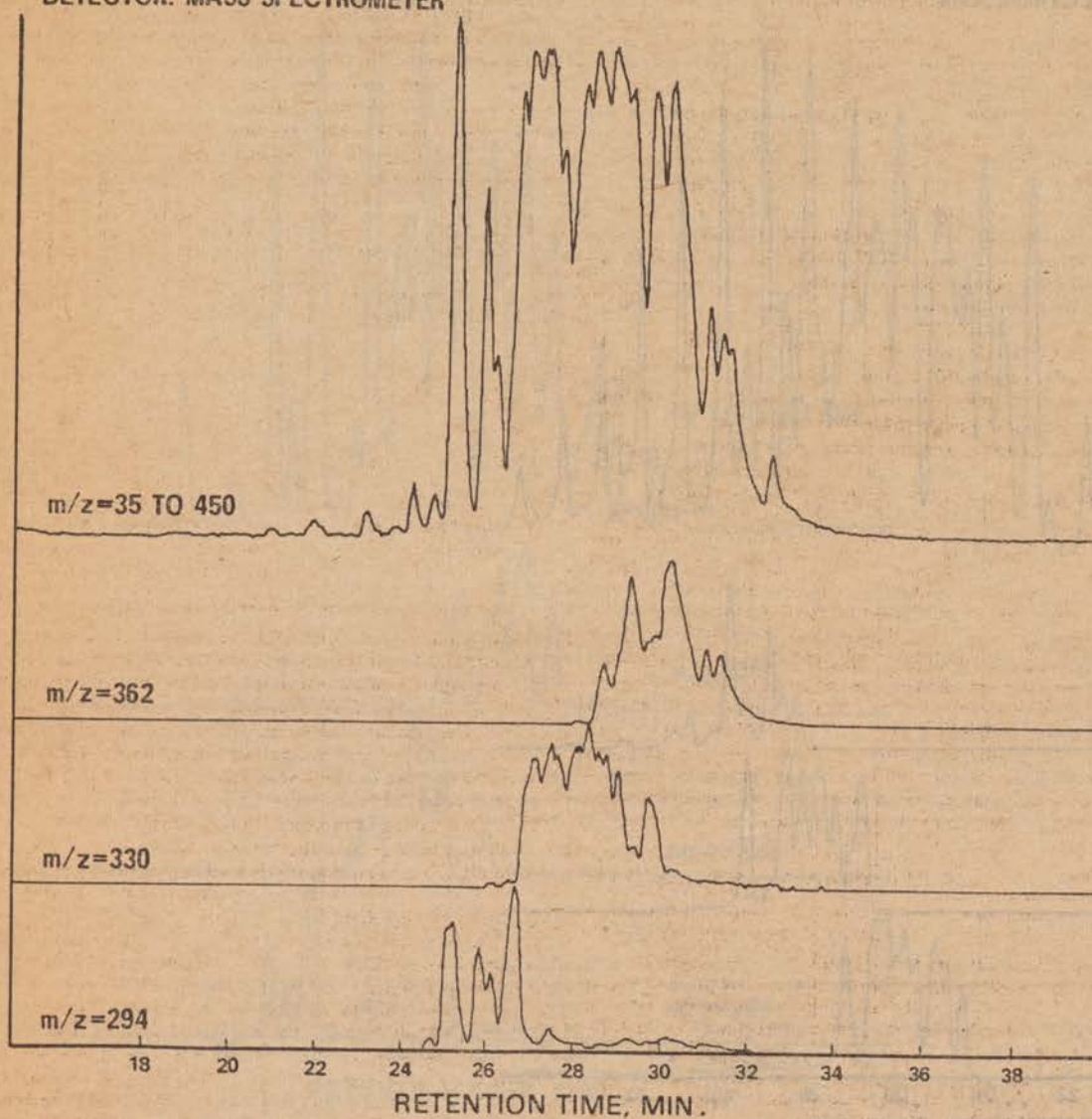


Figure 11. Gas chromatogram of PCB-1254.

COLUMN: 3% SP-2250 ON SUPELCOPORT
PROGRAM: 50°C FOR 4 MIN, 8°C/MIN TO 270°C
DETECTOR: MASS SPECTROMETER

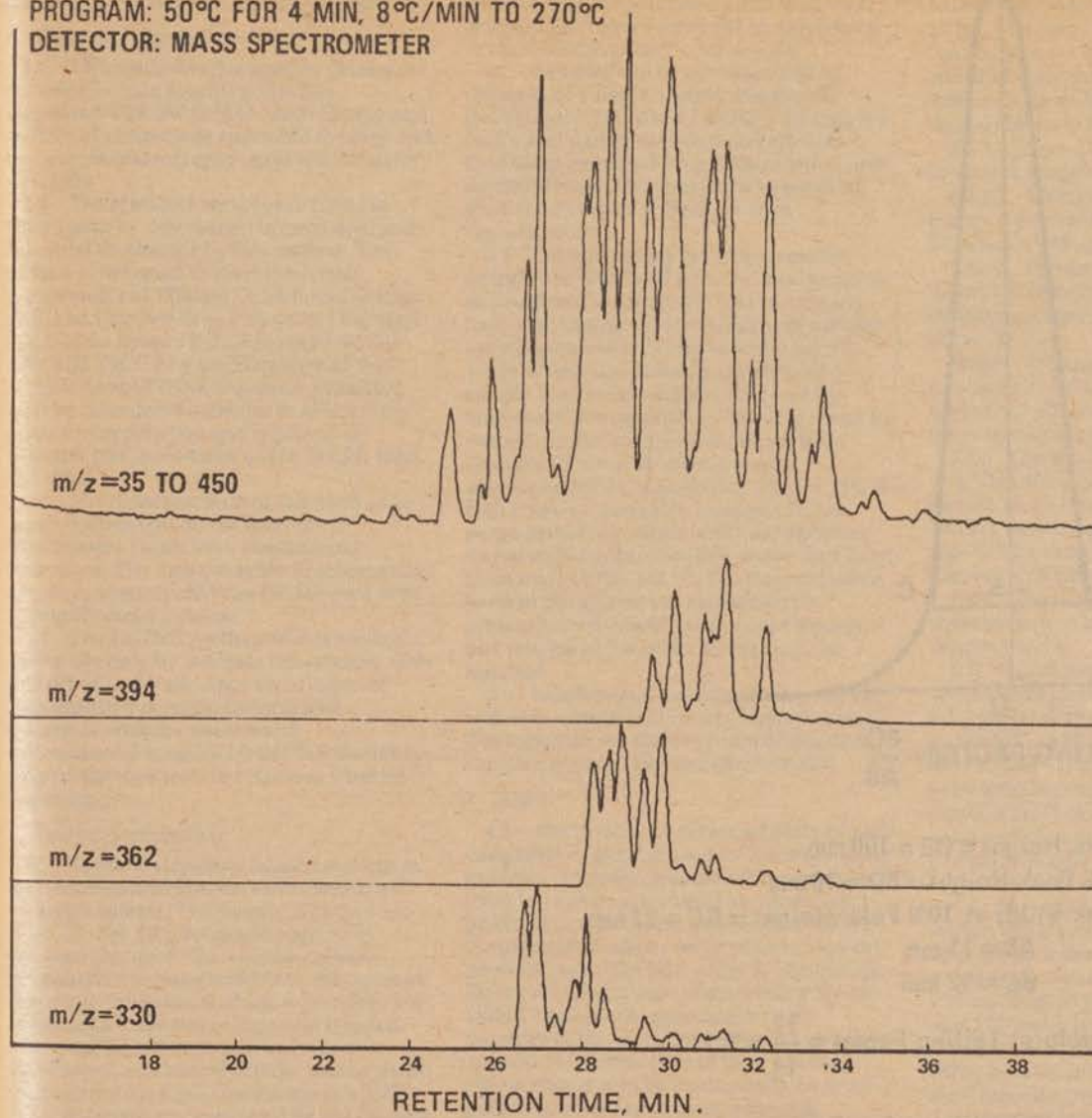
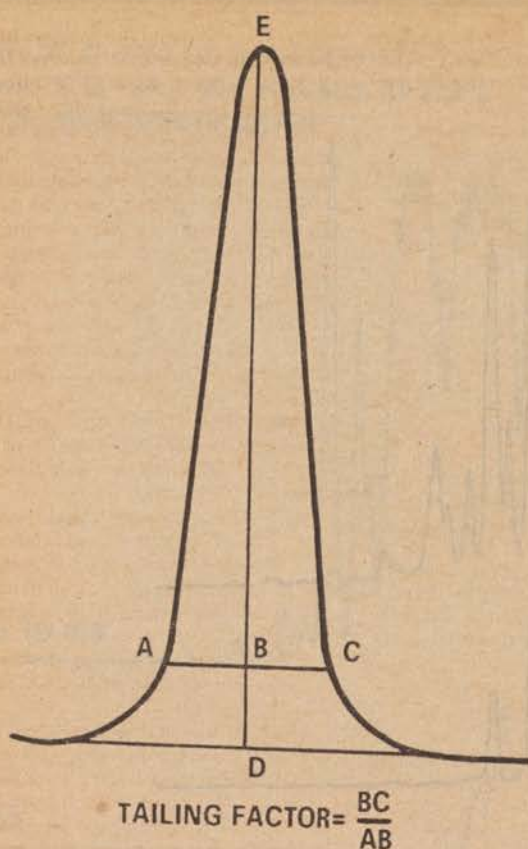


Figure 12. Gas chromatogram of PCB-1260.



Example calculation: Peak Height = DE = 100 mm

10% Peak Height = BD = 10 mm

Peak Width at 10% Peak Height = AC = 23 mm

AB = 11 mm

BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11} = 1.1$

Figure 13. Tailing factor calculation.

Method 1624 Revision B—Volatile Organic Compounds by Isotope Dilution GC/MS

1 Scope and application

1.1 This method is designed to determine the volatile toxic organic pollutants associated with the 1976 Consent Decree and additional compounds amenable to purge and trap gas chromatography-mass spectrometry (GC/MS).

1.2 The chemical compounds listed in table 1 may be determined in municipal and industrial discharges by this method. The method is designed to meet the survey requirements of Effluent Guidelines Division (EGD) and the National Pollutants Discharge Elimination System (NPDES) under 40 CFR 136.1 and 136.5. Any modifications of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits in table 2 represent the minimum quantity that can be detected with no interferences present.

1.4 The GC/MS portions of this method are for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons. Laboratories unfamiliar with the analyses of environmental samples by GC/MS should run the performance tests in reference 1 before beginning.

2 Summary of method

2.1 Stable isotopically labeled analogs of the compounds of interest are added to a 5 mL water sample. The sample is purged at 20–25 °C with an inert gas in a specially designed chamber. The volatile organic compounds are transferred from the aqueous phase into the gaseous phase where they are passed into a sorbent column and trapped. After purging is completed, the trap is backflushed and heated rapidly to desorb the compounds into a gas chromatograph (GC). The compounds are separated by the GC and detected by a mass spectrometer (MS) (references 2 and 3). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a compound (qualitative analysis) is performed by comparing the GC retention time and the background corrected characteristic spectral masses with those of authentic standards.

2.3 Quantitative analysis is performed by GC/MS using extracted ion current profile (EICP) areas. Isotope dilution is used when labeled compounds are available; otherwise, an internal or external standard method is used.

2.4 Quality is assured through reproducible calibration and testing of the purge and trap and GC/MS systems.

3 Contamination and interferences

3.1 Impurities in the purge gas, organic compounds out-gassing from the plumbing upstream of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system is demonstrated to be free from

interferences under conditions of the analysis by analyzing blanks initially and with each sample lot (samples analyzed on the same 8 hr shift), as described in section 8.5.

3.2 Samples can be contaminated by diffusion of volatile organic compounds (particularly methylene chloride) through the bottle seal during shipment and storage. A field blank prepared from reagent water and carried through the sampling and handling protocol serves as a check on such contamination.

3.3 Contamination by carry-over can occur when high level and low level samples are analyzed sequentially. To reduce carry-over, the purging device and sample syringe are rinsed between samples with reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a reagent water blank to check for carry-over. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high levels or purgeable compounds, the purge device is washed with soap solution, rinsed with tap and distilled water, and dried in an oven at 100–125 °C. The trap and other parts of the system are also subject to contamination; therefore, frequent bakeout and purging of the entire system may be required.

3.4 Interferences resulting from samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being sampled.

4 Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 4–6.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, chloroform, and vinyl chloride. Primary standards of these toxic compounds should be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 Apparatus and materials

5.1 Sample bottles for discrete sampling

5.1.1 Bottle—25 to 40 mL with screw cap (Pierce 13075, or equivalent). Detergent wash, rinse with tap and distilled water, and dry at >105 °C for one hr minimum before use.

5.1.2 Septum—Teflon-faced silicone (Pierce 12722, or equivalent), cleaned as above and baked at 100–200 °C, for one hour minimum.

5.2 Purge and trap device—consists of purging device, trap, and desorber. Complete devices are commercially available.

5.2.1 Purging device—designed to accept 5 mL samples with water column at least 3 cm

deep. The volume of the gaseous head space between the water and trap shall be less than 15 mL. The purge gas shall be introduced less than 5 mm from the base of the water column and shall pass through the water as bubbles with a diameter less than 3 mm. The purging device shown in figure 1 meets these criteria.

5.2.2 Trap—25 to 30 cm x 2.5 mm i.d. minimum, containing the following:

5.2.2.1 Methyl silicone packing—one ± 0.2 cm, 3 percent OV-1 on 60/80 mesh Chromosorb W, or equivalent.

5.2.2.2 Porous polymer—15 ± 1.0 cm, Tenax GC (2,6-diphenylene oxide polymer), 60/80 mesh, chromatographic grade, or equivalent.

5.2.2.3 Silica gel—8 ± 1.0 cm, Davison Chemical, 35/60 mesh, grade 15, or equivalent. The trap shown in figure 2 meets these specifications.

5.2.3 Desorber—shall heat the trap to 175 ± 5 °C in 45 seconds or less. The polymer section of the trap shall not exceed 180 °C, and the remaining sections shall not exceed 220 °C. The desorber shown in figure 2 meets these specifications.

5.2.4 The purge and trap device may be a separate unit or coupled to a GC as shown in figures 3 and 4.

5.3 Gas chromatograph—shall be linearly temperature programmable with initial and final holds, shall contain a glass jet separator as the MS interface, and shall produce results which meet the calibration (section 7), quality assurance (section 8), and performance tests (section 11) of this method.

5.3.1 Column—2.8 ± 0.4 m x 2 ± 0.5 mm i.d. glass, packed with one percent SP-1000 on Carbowax B, 60/80 mesh, or equivalent.

5.4 Mass spectrometer—70 eV electron impact ionization; shall repetitively scan from 20 to 250 amu every 2–3 seconds, and produce a unit resolution (valleys between m/z 174–176 less than 10 percent of the height of the m/z 175 peak), background corrected mass spectrum from 50 ng 4-bromo-fluorobenzene (BFB) injected into the GC. The BFB spectrum shall meet the mass-intensity criteria in table 3. All portions of the GC column, transfer lines, and separator which connect the GC column to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.5 Data system—shall collect and record MS data, store mass intensity data in spectral libraries, process GC/MS data and generate reports, and shall calculate and record response factors.

5.5.1 Data acquisition—mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.5.2 Mass spectral libraries—user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse search GC/MS runs for the compounds of interest (section 7.2).

5.5.3 Data processing—the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GC/MS analysis. Software routines shall be employed to compute retention times and EICP areas. Displays of spectra, mass

chromatograms, and library comparisons are required to verify results.

5.5.4 Response factors and multipoint calibrations—the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and generate multi-point calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial and on-going performance shall be maintained (sections 8 and 11).

5.6 Syringes—5 mL glass hypodermic, with Luer-lok tips.

5.7 Micro syringes—10, 25, and 100 μ L.

5.8 Syringe valves—2-way, with Luer ends (Teflon or Kel-F).

5.9 Syringe—5 mL, gas-tight, with shut-off valve.

5.10 Bottles—15 mL, screw-cap with Teflon liner.

5.11 Balance—analytical, capable of weighing 0.1 mg.

6 Reagents and standards

6.1 Reagent water—water in which the compounds of interest and interfering compounds are not detected by this method (section 11.7). It may be generated by any of the following methods:

6.1.1 Activated carbon—pass tap water through a carbon bed (Calgon Filtrasorb-300, or equivalent).

6.1.2 Water purifier—pass tap water through a purifier (Millipore Super Q, or equivalent).

6.1.3 Boil and purge—heat tap water to 90–100 °C and bubble contaminant free inert gas through it for approx one hour. While still hot, transfer the water to screw-cap bottles and seal with a Teflon-lined cap.

6.2 Sodium thiosulfate—ACS granular.

6.3 Methanol—pesticide quality or equivalent.

6.4 Standard solutions—purchased as solution or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to calculate the concentration of the standard.

6.5 Preparation of stock solutions—prepare in methanol using liquid or gaseous standards per the steps below. Observe the safety precautions given in section 4.

6.5.1 Place approx 9.8 mL of methanol in a 10 mL ground glass stoppered volumetric flask. Allow the flask to stand unstoppered for approximately 10 minutes or until all methanol wetted surfaces have dried. In each case, weigh the flask, immediately add the compound, then immediately reweigh to prevent evaporation losses from affecting the measurement.

6.5.1.1 Liquids—using a 100 μ L syringe, permit 2 drops of liquid to fall into the methanol without contacting the neck of the flask. Alternatively, inject a known volume of the compound into the methanol in the flask using a micro-syringe.

6.5.1.2 Gases (chloromethane, bromomethane, chloroethane, vinyl chloride)—fill a valved 5 mL gas-tight syringe with the compound. Lower the needle to approx 5 mm above the methanol meniscus.

Slowly introduce the compound above the surface of the meniscus. The gas will dissolve rapidly in the methanol.

6.5.2 Fill the flask to volume, stopper, then mix by inverting several times. Calculate the concentration in mg/mL (μ g/ μ L) from the weight gain (or density if a known volume was injected).

6.5.3 Transfer the stock solution to a Teflon sealed screw-cap-bottle. Store, with minimal headspace, in the dark at –10 to –20 °C.

6.5.4 Prepare fresh standards weekly for the gases and 2-chloroethylvinyl ether. All other standards are replaced after one month, or sooner if comparison with check standards indicate a change in concentration. Quality control check standards that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

6.6 Labeled compound spiking solution—from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution to contain a concentration such that a 5–10 μ L spike into each 5 mL sample, blank, or aqueous standard analyzed will result in a concentration of 20 μ g/L of each labeled compound. For the gases and for the water soluble compounds (acrolein, acrylonitrile, acetone, diethyl ether, and MEK), a concentration of 100 μ g/L may be used. Include the internal standards (section 7.5) in this solution so that a concentration of 20 μ g/L in each sample, blank, or aqueous standard will be produced.

6.7 Secondary standards—using stock solutions, prepare a secondary standard in methanol to contain each pollutant at a concentration of 500 μ g/mL. For the gases and water soluble compounds (section 6.6), a concentration of 2.5 mg/mL may be used.

6.7.1 Aqueous calibration standards—using a 25 μ L syringe, add 20 μ L of the secondary standard (section 6.7) to 50, 100, 200, 500, and 1000 mL of reagent water to produce concentrations of 200, 100, 50, 20, and 10 μ g/L, respectively. If the higher concentration standard for the gases and water soluble compounds was chosen (section 6.6), these compounds will be at concentrations of 1000, 500, 250, 100, and 50 μ g/L in the aqueous calibration standards.

6.7.2 Aqueous performance standard—an aqueous standard containing all pollutants, internal standards, labeled compounds, and BFB is prepared daily, and analyzed each shift to demonstrate performance (section 11). This standard shall contain either 20 or 100 μ g/L of the labeled and pollutant gases and water soluble compounds, 10 μ g/L BFB, and 20 μ g/L of all other pollutants, labeled compounds, and internal standards. It may be the nominal 20 μ g/L aqueous calibration standard (section 6.7.1).

6.7.3 A methanolic standard containing all pollutants and internal standards is prepared to demonstrate recovery of these compounds when syringe injection and purge and trap analyses are compared. This standard shall contain either 100 μ g/mL or 500 μ g/mL of the gases and water soluble compounds, and 100 μ g/mL of the remaining pollutants and internal standards (consistent

with the amounts in the aqueous performance standard in 6.7.2).

6.7.4 Other standards which may be needed are those for test of BFB performance (section 7.1) and for collection of mass spectra for storage in spectral libraries (section 7.2).

7 Calibration

7.1 Assemble the gas chromatographic apparatus and establish operating conditions given in table 2. By injecting standards into the GC, demonstrate that the analytical system meets the detection limits in table 2 and the mass-intensity criteria in table 3 for 50 ng BFB.

7.2 Mass spectral libraries—detection and identification of the compound of interest are dependent upon the spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each pollutant and labeled compound and each internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound. Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic m/z's or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under BFB tuning conditions (section 7.1 and table 3) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. This spectrum is stored for reverse search and for compound confirmation.

7.3 Assemble the purge and trap device. Pack the trap as shown in figure 2 and condition overnight at 170–180 °C by backflushing with an inert gas at a flow rate of 20–30 mL/min. Condition traps daily for a minimum of 10 minutes prior to use.

7.3.1 Analyze the aqueous performance standard (section 6.7.2) according to the purge and trap procedure in section 10. Compute the area at the primary m/z (table 4) for each compound. Compare these areas to those obtained by injecting one μ L of the methanolic standard (section 6.7.3) to determine compound recovery. The recovery shall be greater than 20 percent for the water soluble compounds, and 60–110 percent for all other compounds. This recovery is demonstrated initially for each purge and trap GC/MS system. The test is repeated only if the purge and trap or GC/MS systems are modified in any way that might result in a change in recovery.

7.3.2 Demonstrate that 100 ng toluene (or toluene-d8) produces an area at m/z 91 (or 99) approx one-tenth that required to exceed

the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required.

7.4 Calibration by isotope dilution—the isotope dilution approach is used for the purgeable organic compounds when appropriate labeled compounds are available and when interferences do not preclude the analysis. If labeled compounds are not available, or interferences are present, internal or external standard methods (section 7.5 or 7.6) are used. A calibration curve encompassing the concentration range of interest is prepared for each compound determined. The relative response (RR) vs concentration ($\mu\text{g/L}$) is plotted or computed using a linear regression. An example of a calibration curve for toluene using toluene-d8 is given in figure 5. Also shown are the ± 10 percent error limits (dotted lines). Relative response is determined according to the procedures described below. A minimum of five data points are required for calibration (section 7.4.4).

7.4.1 The relative response (RR) of pollutant to labeled compound is determined from isotope ratio values calculated from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured in the pure pollutant (figure 6A).

R_y = the isotope ratio of pure labeled compound (figure 6B).

R_m = the isotope ratio measured in the analytical mixture of the pollutant and labeled compounds (figure 6C).

The correct way to calculate RR is:
 $RR = (R_y - R_m) / (R_x - R_m) \times (R_x + 1) / (R_y + 1)$ If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by internal or external standard methods (section 7.5 or 7.6).

7.4.2 In most cases, the retention times of the pollutant and labeled compound are the same and isotope ratios (R 's) can be calculated from the EICP areas, where:
 $R = (\text{area at } m_1/z) / (\text{area at } m_2/z)$ If either of the areas is zero, it is assigned a value of one in the calculations; that is, if area of $m_1/z = 50721$, and area of $m_2/z = 0$, then $R = 50721/1 = 50720$. The m/z 's are always selected such that $R_x > R_y$. When there is a difference in retention times (RT) between the pollutant and labeled compounds, special precautions are required to determine the isotope ratios.

R_x , R_y , and R_m are defined as follows:

$R_x = [\text{area } m_1/z \text{ (at } RT_1)] / 1$

$R_y = 1 / [\text{area } m_2/z \text{ (at } RT_2)]$

$R_m = [\text{area } m_1/z \text{ (at } RT_1)] / [\text{area } m_2/z \text{ (at } RT_2)]$

7.4.3 An example of the above calculations can be taken from the data plotted in figure 5 for toluene and toluene-d8. For these data, $R_x = 168920/1 = 168900$, $R_y = 1/60960 = 0.00001640$, and $R_m = 96868/82508 = 1.174$. The RR for the above data is then calculated using the equation given in section 7.4.1. For the example, $RR = 1.174$.
 Note: Not all labeled compounds elute before their pollutant analogs.

7.4.4 To calibrate the analytical system by isotope dilution, analyze a 5 mL aliquot of

each of the aqueous calibration standards (section 6.7.1) spiked with an appropriate constant amount of the labeled compound spiking solution (section 6.6), using the purge and trap procedure in section 10. Compute the RR at each concentration.

7.4.5 Linearity—if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, an averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard—used when criteria for isotope dilution (section 7.4) cannot be met. The method is applied to pollutants having no labeled analog and to the labeled compounds. The internal standards used for volatiles analyses are bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane. Concentrations of the labeled compounds and pollutants without labeled analogs are computed relative to the nearest eluted internal standard, as shown in table 2.

7.5.1 Response factors—calibration requires the determination of response factors (RF) which are defined by the following equation: $RF = (A_x \times C_{is}) / (A_{is} \times C_x)$, where A_x is the EICP area at the characteristic m/z for the compound in the daily standard, A_{is} is the EICP area at the characteristic m/z for the internal standard.

C_{is} is the concentration ($\mu\text{g/L}$) of the internal standard

C_x is the concentration of the pollutant in the daily standard.

7.5.2 The response factor is determined at 10, 20, 50, 100, and 200 $\mu\text{g/L}$ for the pollutants (optionally at five times these concentrations for gases and water soluble pollutants—see section 6.7), in a way analogous to that for calibration by isotope dilution (section 7.4.4). The RF is plotted against concentration for each compound in the standard (C_x) to produce a calibration curve.

7.5.3 Linearity—if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration—by adding the isotopically labeled compounds and internal standards (section 6.6) to the aqueous calibration standards (section 6.7.1), a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 11.5) by purging the aqueous performance standard (section 6.7.2). Recalibration is required only if calibration and on-going performance (section 11.5) criteria cannot be met.

8 Quality assurance/quality control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled

compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance.

Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis (section 3). The procedures and criteria for analysis of a blank are described in sections 8.5 and 11.7.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring method performance within acceptable limits (section 14.2).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through the analysis of the aqueous performance standard (section 6.7.2) that the analysis system is in control. This procedure is described in sections 11.1 and 11.5.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in sections 8.4 and 11.5.2.

8.2 Initial precision and accuracy—to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 Analyze two sets of four 5-mL aliquots (8 aliquots total) of the aqueous performance standard (section 6.7.2) according to the method beginning in section 10.

8.2.2 Using results of the first set of four analyses in section 8.2.1, compute the average recovery ($\bar{X}$) in $\mu\text{g/L}$ and the standard deviation of the recovery (s) in $\mu\text{g/L}$ for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and $\bar{X}$ with the corresponding limits for initial precision and accuracy found in table 5. If s and $\bar{X}$ for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If individual $\bar{X}$ falls outside the range for accuracy, system performance is unacceptable for that compound. NOTE: The large number of compounds in table 5 present a substantial probability that one or more will fail one of the acceptance criteria when

all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and $\bar{X}$ for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for the compound(s) in question. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Spike and analyze each sample according to the method beginning in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the percent recovery for each compound with the corresponding labeled compound recovery limit in table 5. If the recovery of any compound falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample matrix is complex and the sample is to be diluted and reanalyzed, per section 14.2.

8.4 As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in section 8.3.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if $P = 90\%$ and $s_p = 10\%$, the accuracy interval is expressed as 70–110%. Update the accuracy assessment for each compound on a regular basis (e.g. after each 5–10 new accuracy measurements).

8.5 Blanks—reagent water blanks are analyzed to demonstrate freedom from carry-over (section 3) and contamination.

8.5.1 The level at which the purge and trap system will carry greater than $5 \mu\text{g/L}$ of a pollutant of interest (table 1) into a succeeding blank shall be determined by analyzing successively larger concentrations of these compounds. When a sample contains this concentration or more, a blank shall be analyzed immediately following this sample to demonstrate no carry-over at the $5 \mu\text{g/L}$ level.

8.5.2 With each sample lot (samples analyzed on the same 8 hr shift), a blank shall be analyzed immediately after analysis of the aqueous performance standard (section 11.1) to demonstrate freedom from contamination. If any of the compounds of interest (table 1) or any potentially interfering compound is found in a blank at greater than $10 \mu\text{g/L}$ (assuming a response factor of 1 relative to the nearest eluted internal standard for compounds not listed in table 1), analysis of samples is halted until the source of contamination is eliminated and a blank

shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state.

The standards used for calibration (section 7), calibration verification (section 11.5) and for initial (section 8.2) and on-going (section 11.5) precision and accuracy should be identical, so that the most precise results will be obtained. The GC/MS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when internal or external standard methods are used.

9 Sample collection, preservation, and handling

9.1 Grab samples are collected in glass containers having a total volume greater than 20 mL. Fill sample bottles so that no air bubbles pass through the sample as the bottle is filled. Seal each bottle so that no air bubbles are entrapped. Maintain the hermetic seal on the sample bottle until time of analysis.

9.2 Samples are maintained at 0–4 °C from the time of collection until analysis. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 mg/40 mL) to the empty sample bottles just prior to shipment to the sample site. EPA Methods 330.4 and 330.5 may be used for measurement of residual chlorine (reference 8). If preservative has been added, shake bottle vigorously for one minute immediately after filling.

9.3 Experimental evidence indicates that some aromatic compounds, notably benzene, toluene, and ethyl benzene are susceptible to rapid biological degradation under certain environmental conditions. Refrigeration alone may not be adequate to preserve these compounds in wastewaters for more than seven days. For this reason, a separate sample should be collected, acidified, and analyzed when these aromatics are to be determined. Collect about 500 mL of sample in a clean container.

Adjust the pH of the sample to about 2 by adding HCl (1+1) while stirring. Check pH with narrow range (1.4 to 2.8) pH paper. Fill a sample container as described in section 9.1. If residual chlorine is present, add sodium thiosulfate to a separate sample container and fill as in section 9.1.

9.4 All samples shall be analyzed within 14 days of collection.

10 Purge, trap, and GC/MS analysis

10.1 Remove standards and samples from cold storage and bring to 20–25 °.

10.2 Adjust the purge gas flow rate to $40 \pm 4 \text{ mL/min}$. Attach the trap inlet to the purging device and set the valve to the purge mode (figure 3). Open the syringe valve located on the purging device sample introduction needle (figure 1).

10.3 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample bottle and carefully pour the sample into the syringe barrel until it overflows. Replace the plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Because this process of taking an aliquot destroys the validity of the sample for future analysis, fill a second syringe at this time to protect against possible loss of data. Add an appropriate amount of the labeled compound spiking solution (section 6.6) through the valve bore, then close the valve.

10.4 Attach the syringe valve assembly to the syringe valve on the purging device. Open both syringe valves and inject the sample into the purging chamber.

10.5 Close both valves and purge the sample for 11.0 ± 0.1 minutes at 20–25 °C.

10.6 After the 11 minute purge time, attach the trap to the chromatograph and set the purge and trap apparatus to the desorb mode (figure 4). Desorb the trapped compounds into the GC column by heating the trap to 170–180 °C while backflushing with carrier gas at 20–60 mL/min for four minutes. Start MS data acquisition upon start of the desorb cycle, and start the GC column temperature program 3 minutes later. Table 1 summarizes the recommended operating conditions for the gas chromatograph. Included in this table are retention times and detection limits that were achieved under these conditions. An example of the separations achieved by the column listed is shown in figure 5. Other columns may be used provided the requirements in section 8 can be met. If the priority pollutant gases produce GC peaks so broad that the precision and recovery specifications (section 8.2) cannot be met, the column may be cooled to ambient or sub-ambient temperatures to sharpen these peaks.

10.7 While analysis of the desorbed compounds proceeds, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-mL portions of reagent water. After the purging device has been emptied, allow the purge gas to vent through the chamber until the frit is dry, so that it is ready for the next sample.

10.8 After desorbing the sample for four minutes, recondition the trap by returning to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 170–180 °C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

11 System performance

11.1 At the beginning of each 8 hr shift during which analyses are performed, system calibration and performance shall be verified for all pollutants and labeled compounds. For these tests, analysis of the aqueous performance standard (section 6.7.2) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance

criteria are met may blanks and samples be analyzed.

11.2 BFB spectrum validity—the criteria in table 3 shall be met.

11.3 Retention times—the absolute retention times of all compounds shall approximate those given in table 2.

11.4 GC resolution—the valley height between toluene and toluene-d8 (at m/z 91 and 99 plotted on the same graph) shall be less than 10 percent of the taller of the two peaks.

11.5 Calibration verification and on-going precision and accuracy—compute the concentration of each pollutant (table 1) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant (table 1) which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

11.5.1 For each pollutant and labeled compound, compare the concentration with the corresponding limit for on-going accuracy in table 5. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue. If any individual value falls outside the range given, system performance is unacceptable for that compound. NOTE: The large number of compounds in table 5 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure may be attributed to probability, proceed as follows:

11.5.1.1 Analyze a second aliquot of the aqueous performance standard (section 6.7.2).

11.5.1.2 Compute the concentration for only those compounds which failed the first test (section 11.5.1). If these compounds now pass, system performance is acceptable for all compounds and analyses of blanks and samples may proceed. If, however, any of the compounds fail again, the measurement system is not performing properly for these compounds. In this event, locate and correct the problem or recalibrate the system (section 7), and repeat the entire test (section 11.1) for all compounds.

11.5.2 Add results which pass the specification in 11.5.1.2 to initial (section 8.2) and previous on-going data. Update QC charts to form a graphic representation of laboratory performance (Figure 7). Develop a statement of accuracy for each pollutant and labeled compound by calculating the average percentage recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from $R-2s_r$ to $R+2s_r$. For example, if $R=95\%$ and $s_r=5\%$, the accuracy is 85–105 percent.

12 Qualitative determination—accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (section 11.1). Identification is confirmed when spectra and retention times agree per the criteria below.

12.1 Labeled compounds and pollutants having no labeled analog:

12.1.1 The signals for all characteristic masses stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.1.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

12.1.3 The retention time relative to the nearest eluted internal standard shall be within ± 7 scans or ± 20 seconds, whichever is greater.

12.2 Pollutants having a labeled analog:

12.2.1 The signals for all characteristic masses stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

12.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

12.2.3 The retention time difference between the pollutant and its labeled analog shall agree within ± 2 scans or ± 6 seconds (whichever is greater) of this difference in the shift standard (section 11.1).

12.3 Masses present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

13 Quantitative determination

13.1 Isotope dilution—by adding a known amount of a labeled compound to every sample prior to purging, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon purging, desorption, and gas chromatography. Relative response (RR) values for sample mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the toluene example given in figure 6 (section 7.4.3), RR would be equal to 1.174. For this RR value, the toluene calibration curve given in figure 5 indicates a concentration of 31.8 $\mu\text{g/L}$.

13.2 Internal standard—calculate the concentration using the response factor determined from calibration data (section 7.5) and the following equation:

Concentration = $(A_s \times C_{is}) / (A_{is} \times RF)$ where the terms are as defined in section 7.5.1.

13.3 If the EICP area at the quantitation mass for any compound exceeds the calibration range of the system, the sample is diluted by successive factors of 10 and these dilutions are analyzed until the area is within the calibration range.

13.4 Report results for all pollutants and labeled compounds (table 1) found in all standards, blanks, and samples, in $\mu\text{g/L}$ to three significant figures. Results for samples which have been diluted are reported at the

least dilute level at which the area at the quantitation mass is within the calibration range (section 13.3) and the labeled compound recovery is within the normal range for the Method (section 14.2).

14 Analysis of complex samples

14.1 Untreated effluents and other samples frequently contain high levels ($>1000 \mu\text{g/L}$) of the compounds of interest and of interfering compounds. Some samples will foam excessively when purged; others will overload the trap/or GC column.

14.2 Dilute 0.5 mL of sample with 4.5 mL of reagent water and analyze this diluted sample when labeled compound recovery is outside the range given in table 5. If the recovery remains outside of the range for this diluted sample, the aqueous performance standard shall be analyzed (section 11) and calibration verified (section 11.5). If the recovery for the labeled compound in the aqueous performance standard is outside the range given in table 5, the analytical system is out of control. In this case, the instrument shall be repaired, the performance specifications in section 11 shall be met, and the analysis of the undiluted sample shall be repeated. If the recovery for the aqueous performance standard is within the range given in table 5, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

14.3 Reverse search computer programs can misinterpret the spectrum of chromatographically unresolved pollutant and labeled compound pairs with overlapping spectra when a high level of the pollutant is present. Examine each chromatogram for peaks greater than the height of the internal standard peaks. These peaks can obscure the compounds of interest.

15 Method performance

15.1 The specifications for this method were taken from the inter-laboratory validation of EPA Method 824 (reference 9). Method 824 has been shown to yield slightly better performance on treated effluents than Method 824. Additional method performance data can be found in Reference 10.

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2. Bellar, T.A. and Lichtenberg, J.J., "Journal American Water Works Association," 66, 739 (1974).
3. Bellar, T.A. and Lichtenberg, J.J., "Semi-automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in *Measurement of Organic Pollutants Water and Wastewater*, C.E. VanHallen, ed., American Society for Testing Materials, Philadelphia, PA, Special Technical Publication 686, (1978).
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8. "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL/Cincinnati, OH 45268, EPA-4-79-020 (March 1979).

9. "Test Method: Purgeables—Method 624," USEPA, EMSL/Cincinnati, OH 45268.

10. "Colby, B.N., Beimer, R.G., Rushneck, D.R., and Telliard, W.A., "Isotope Dilution Gas Chromatography-Mass Spectrometry for the Determination of Priority Pollutants in Industrial Effluents," USEPA, Effluent Guidelines Division, Washington, DC 20460 (1980).

TABLE 1.—VOLATILE ORGANIC COMPOUNDS ANALYZED BY ISOTOPE DILUTION GC/MS

Compound	Storet	CAS registry	EPA-EGD	NPDES
Acetone	81552	67-64-1	516 V	
Acrolein	34210	107-02-8	002 V	001 V
Acrylonitrile	34215	107-13-1	003 V	002 V
Benzene	34030	71-43-2	004 V	003 V
Bromodichloromethane	32101	75-27-4	048 V	012 V
Bromoform	32104	75-25-2	047 V	005 V
Bromomethane	34413	74-83-9	048 V	020 V
Carbon tetrachloride	32102	56-23-5	006 V	006 V
Chlorobenzene	34301	108-90-7	007 V	007 V
Chloroethane	34311	75-00-3	016 V	009 V
2-chloroethylvinyl ether	34576	110-75-8	019 V	010 V
Chloroform	32106	67-66-1	023 V	011 V
Chloromethane	34418	74-87-3	045 V	021 V
Dibromochloromethane	32105	124-48-1	051 V	008 V
1,1-dichloroethane	34496	75-34-3	013 V	014 V
1,2-dichloroethane	32103	107-06-2	010 V	015 V
1,1-dichloroethane	34501	75-35-4	029 V	016 V
Trans-1,2-dichloroethane	34546	156-60-5	030 V	026 V
1,2-dichloropropane	34541	78-87-5	032 V	017 V
Cis-1,3-dichloropropene	34704	10061-01-5		
Trans-1,3-dichloropropene	34699	10061-02-6	033 V	
Diethyl ether	81576	60-29-7	515 V	
p-dioxane	81582	123-91-1	527 V	
Ethylbenzene	34371	100-41-4	038 V	019 V
Methylene chloride	34423	75-09-2	044 V	022 V
Methyl ethyl ketone	81595	78-93-3	514 V	
1,1,2,2-tetrachloroethane	34516	79-34-5	015 V	023 V
Tetrachloroethane	34475	127-18-4	085 V	024 V
Toluene	34010	108-88-3	086 V	025 V
1,1,1-trichloroethane	34506	71-55-6	011 V	027 V
1,1,2-trichloroethane	34511	79-00-5	014 V	028 V
Trichloroethane	39130	79-01-6	087 V	029 V
Vinyl chloride	39175	75-01-4	088 V	031 V

TABLE 2.—GAS CHROMATOGRAPHY OF PURGEABLE ORGANIC COMPOUNDS BY ISOTOPE DILUTION GC/MS

EGD No. (1)	Compound	Ref EGD No.	Mean retention time (sec)	Minimum level (2) (µg/L)
181	Bromochloromethane (I.S.)	181	730	10
245	Chloromethane-d3	181	147	50
345	Chloromethane	245	148	50
248	Bromomethane-d3	181	243	50
346	Bromomethane	248	246	50
288	Vinyl chloride-d3	181	301	50
388	Vinyl chloride	288	304	10
216	Chloroethane-d5	181	378	50
316	Chloroethane	216	386	50
244	Methylene chloride-d2	181	512	10
344	Methylene chloride	244	517	10
616	Acetone-d6	181	554	50
716	Acetone	616	565	50
002	Acrolein	181	586	50
203	Acrylonitrile-d3	181	606	50
303	Acrylonitrile	203	612	50
229	1,1-dichloroethane-d2	181	696	10
329	1,1-dichloroethane	229	698	10
213	1,1-dichloroethane-d3	181	778	10
313	1,1-dichloroethane	213	796	10
615	Diethyl ether-d10	181	804	50
715	Diethyl ether	615	820	50
230	Trans-1,2-dichloroethane-d2	181	821	10
330	Trans-1,2-dichloroethane	230	821	10
614	Methyl ethyl ketone-d3	181	840	50
714	Methyl ethyl ketone	614	848	50
223	Chloroform-13C1	181	861	10
323	Chloroform	223	861	10
210	1,2-dichloroethane-d4	181	901	10
310	1,2-dichloroethane	210	910	10
211	1,1,1-trichloroethane-13C2	181	989	10
311	1,1,1-trichloroethane	211	999	10
527	p-dioxane	181	1001	10
206	Carbon tetrachloride-13C1	182	1018	10
306	Carbon tetrachloride	206	1018	10
248	Bromodichloromethane-13C1	182	1045	10
348	Bromodichloromethane	248	1045	10
232	1,2-dichloropropane-d6	182	1123	10
332	1,2-dichloropropane	232	1134	10
233	Trans-1,3-dichloropropene-d4	182	1138	10
333	Trans-1,3-dichloropropene	233	1138	10
287	Trichloroethene-13C1	182	1172	10
387	Trichloroethene	287	1187	10
204	Benzene-d6	182	1200	10
304	Benzene	204	1212	10
251	Chlorodibromomethane-13C1	182	1222	10
351	Chlorodibromomethane	251	1222	10
214	1,1,2-trichloroethane-13C2	182	1224	10
314	1,1,2-trichloroethane	214	1224	10
019	2-chloroethylvinyl ether	182	1278	10
182	2-bromo-1-chloropropane (I.S.)	182	1306	10
247	Bromoform-13C1	182	1386	10
347	Bromoform	247	1386	10
215	1,1,2,2-tetrachloroethane-d2	183	1525	10
315	1,1,2,2-tetrachloroethane	215	1525	10
285	Tetrachloroethene-13C2	183	1528	10
385	Tetrachloroethene	285	1528	10
183	1,4-dichlorobutane (int std)	183	1555	10
286	Toluene-d8	183	1603	10
386	Toluene	286	1619	10
207	Chlorobenzene-d5	183	1679	10
307	Chlorobenzene	207	1679	10
238	Ethylbenzene-d10	183	1802	10
338	Ethylbenzene	238	1820	10
185	Bromofluorobenzene	183	1985	10

(1) Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

(2) This is a minimum level at which the analytical system shall give recognizable mass spectra (background corrected) and acceptable calibration points. Column: 2.4m (8 ft) x 2 mm i.d. glass, packed with one percent SP-1000 coated on 60/80 Carbowax B. Carrier gas: helium at 40 mL/min. Temperature program: 3 min at 45 °C, 8 °C per min to 240 °C, hold at 240 °C for 15 minutes.

Note.—The specifications in this table were developed from data collected from three wastewater laboratories.

TABLE 3.—BFB Mass-Intensity Specifications

Mass	Intensity required
50	15 to 40 percent of mass 95.
75	30 to 60 percent of mass 95.
95	base peak, 100 percent.
96	5 to 9 percent of mass 95.
173	<2 percent of mass 174.
174	>50 percent of mass 95.
176	95 to 100 percent of mass 174.
177	5 to 9 percent of mass 176.

TABLE 4.—VOLATILE ORGANIC COMPOUND CHARACTERISTIC MASSES

Labeled compound	Analog	Primary m/z's
Acetone	d6	58/64
Acrolein	d2	56/58
Acrylonitrile	d3	53/56
Benzene	d6	78/84
Bromodichloromethane	13C	83/86
Bromoform	13C	173/176
Bromomethane	d3	96/99
Carbon tetrachloride	13C	147/148
Chlorobenzene	d5	112/117
Chloroethane	d5	64/71
2-chloroethylvinyl ether	d7	106/113
Chloroform	13C	85/86
Chloromethane	d3	50/53
Dibromochloromethane	13C	129/130
1,1-dichloroethane	d3	63/66
1,2-dichloroethane	d4	62/67
1,1-dichloroethane	d2	61/65
Trans-1,2-dichloroethane	d2	61/65
1,2-dichloropropane	d6	63/67
Cis-1,3-dichloropropene	d4	75/79
Trans-1,3-dichloropropene	d4	75/79
Diethyl ether	d10	74/84
p-dioxane	d8	88/96
Ethylbenzene	d10	106/116
Methylene chloride	d2	84/88
Methyl ethyl ketone	d3	72/75
1,1,2,2-tetrachloroethane	d2	83/84
Tetrachloroethene	13C2	166/172
Toluene	d8	92/99
1,1,1-trichloroethane	d3	97/102
1,1,2-trichloroethane	13C2	83/84
Trichloroethene	13C	95/133
Vinyl chloride	d3	62/65

TABLE 5.—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

Compound	Acceptance criteria at 20 µg/L			
	Initial precision and accuracy section 8.2.3		Labeled compound recovery sec 8.3 and 14.2	On-going accuracy sec 11.5
	s (µg/L)	$\bar{x}$ (µg/L)	P (percent)	R (µg/L)
Acetone.....			note 1	
Acrolein.....			note 2	
Acrylonitrile.....			note 2	
Benzene.....	9.0	13.0-28.2	ns-196	4-33
Bromodichloromethane.....	8.2	6.5-31.5	ns-199	4-34
Bromoform.....	7.0	7.4-35.1	ns-214	6-36
Bromomethane.....	25.0	d-54.3	ns-414	d-61
Carbon tetrachloride.....	6.9	15.9-24.8	42-165	12-30
Chlorobenzene.....	8.2	14.2-29.6	ns-205	4-35
Chloroethane.....	14.8	2.1-46.7	ns-308	d-51
2-chloroethylvinyl ether.....	36.0	d-69.8	ns-554	d-79
Chloroform.....	7.9	11.6-26.3	18-172	8-30
Chloromethane.....	26.0	d-55.5	ns-410	d-64
Dibromochloromethane.....	7.9	11.2-29.1	18-185	8-32
1,1-dichloroethane.....	6.7	11.4-31.4	23-191	9-33
1,2-dichloroethane.....	7.7	11.6-30.1	12-192	8-33
1,1-dichloroethene.....	11.7	d-49.8	ns-315	d-52
Trans-1,2-dichloroethene.....	7.4	10.5-31.5	15-195	8-34
1,2-dichloropropane.....	19.2	d-46.8	ns-343	d-51
Cis-1,3-dichloropropene.....	22.1	d-51.0	ns-381	d-56
Trans-1,3-dichloropropene.....	14.5	d-40.2	ns-284	d-44
Diethyl ether.....			note 1	
P-dioxane.....			note 1	
Ethyl benzene.....	9.6	15.6-28.5	ns-203	5-35
Methylene chloride.....	9.7	d-49.8	ns-316	d-50
Methyl ethyl ketone.....			note 1	
1,1,2,2-tetrachloroethane.....	9.6	10.7-30.0	5-199	7-34
Tetrachloroethene.....	6.6	15.1-28.5	31-181	11-32
Toluene.....	6.3	14.5-28.7	4-193	6-33
1,1,1-trichloroethane.....	5.9	10.5-33.4	12-200	8-35
1,1,2-trichloroethane.....	7.1	11.8-29.7	21-184	9-32
Trichloroethene.....	8.9	16.6-29.5	35-196	12-34
Vinyl chloride.....	27.9	d-58.5	ns-452	d-65

d = detected; result must be greater than zero.

ns = no specification; limit would be below detection limit.

Note 1: Specifications not available for these compounds at time of release of this method.

Note 2: Specifications not developed for these compounds; use method 603.

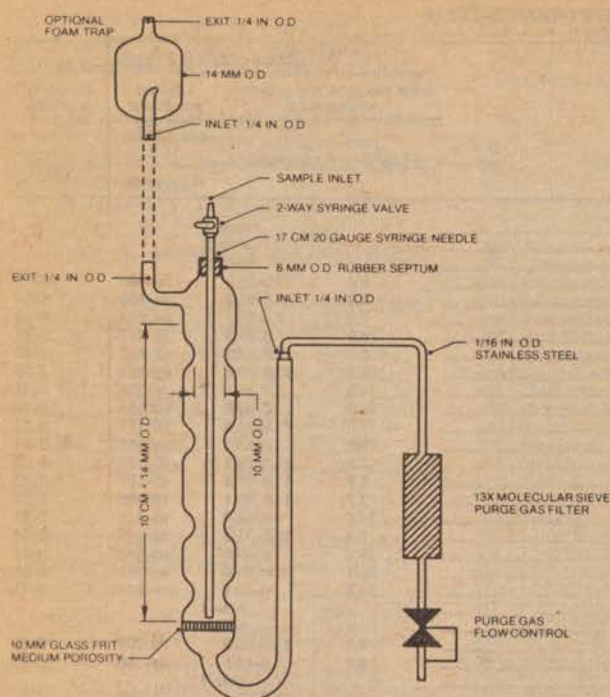


FIGURE 1 Purging Device.

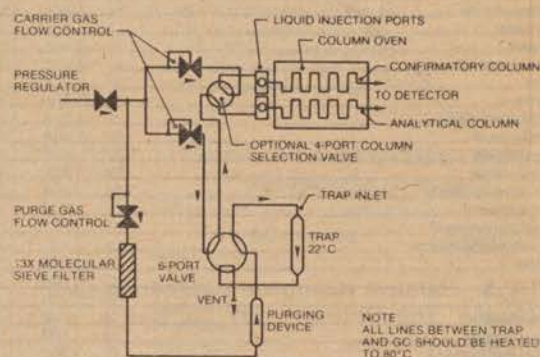


FIGURE 3 Schematic of Purge and Trap Device—Purge Mode.

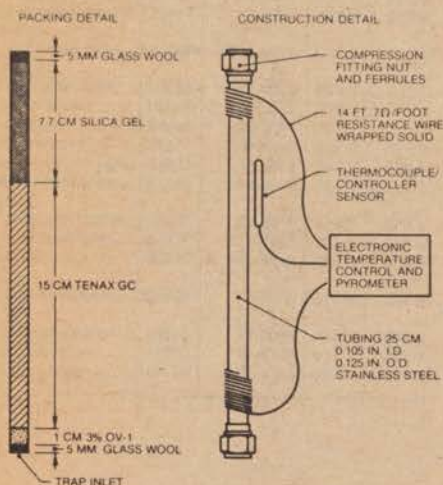


FIGURE 2 Trap Packings and Construction to Include Desorb Capability.

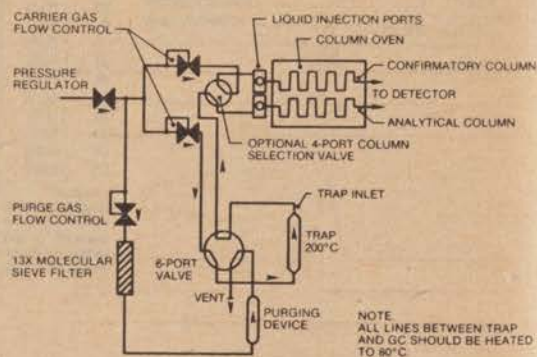


FIGURE 4 Schematic of Purge and Trap Device—Desorb Mode.

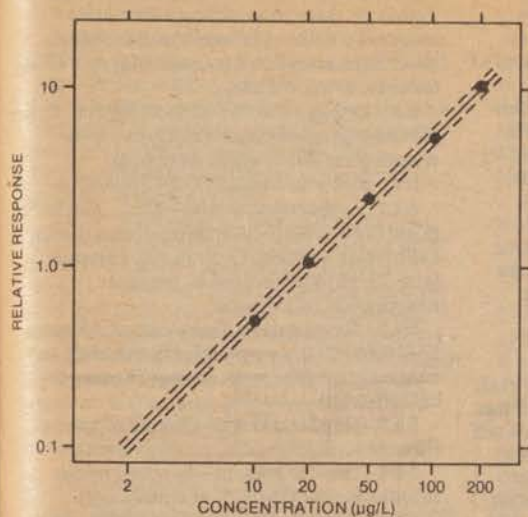


FIGURE 5 Relative Response Calibration Curve for Toluene. The Dotted Lines Enclose a ± 10 Percent Error Window.

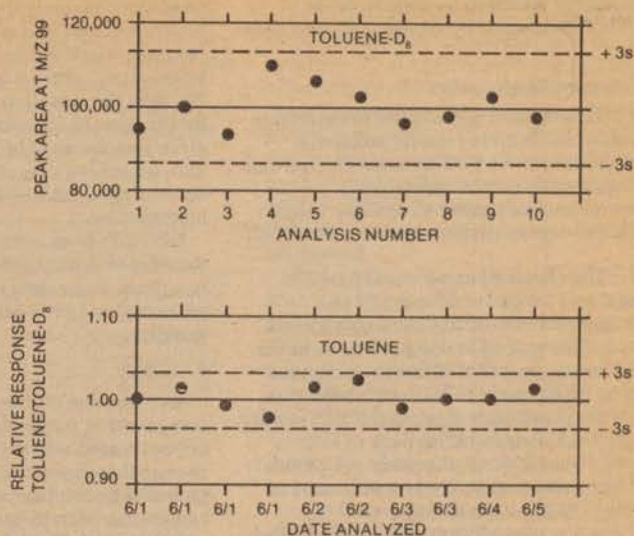


FIGURE 7 Quality Control Charts Showing Area (top graph) and Relative Response of Toluene to Toluene- d_8 (lower graph) Plotted as a Function of Time or Analysis Number.

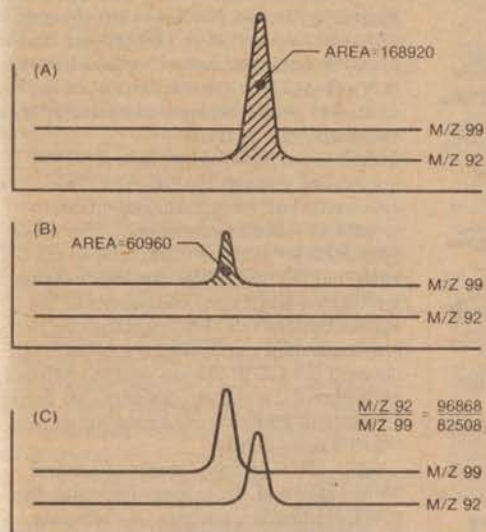


FIGURE 6 Extracted Ion Current Profiles for (A) Toluene, (B) Toluene- d_8 , and a Mixture of Toluene and Toluene- d_8 .

Method 1625 Revision B—Semivolatile Organic Compounds by Isotope Dilution GC/MS

1 Scope and application

1.1 This method is designed to determine the semivolatile toxic organic pollutants associated with the 1976 Consent Decree and additional compounds amenable to extraction and analysis by capillary column gas chromatography-mass spectrometry (GC/MS).

1.2 The chemical compounds listed in tables 1 and 2 may be determined in municipal and industrial discharges by this method. The method is designed to meet the survey requirements of Effluent Guidelines Division (EGD) and the National Pollutants Discharge Elimination System (NPDES) under 40 CFR 136.1. Any modifications of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.3 The detection limit of this method is usually dependent on the level of interferences rather than instrumental limitations. The limits listed in tables 3 and 4 represent the minimum quantity that can be detected with no interferences present.

1.4 The GC/MS portions of this method are for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons. Laboratories unfamiliar with analyses of environmental samples by GC/MS should run the performance tests in reference 1 before beginning.

2 Summary of method

2.1 Stable isotopically labeled analogs of the compounds of interest are added to a one liter wastewater sample. The sample is extracted at pH 12-13, then at pH <2 with methylene chloride using continuous extraction techniques. The extract is dried over sodium sulfate and concentrated to a volume of one mL. An internal standard is added to the extract, and the extract is injected into the gas chromatograph (GC). The compounds are separated by GC and detected by a mass spectrometer (MS). The labeled compounds serve to correct the variability of the analytical technique.

2.2 Identification of a compound (qualitative analysis) is performed by comparing the GC retention time and background corrected characteristic spectral masses with those of authentic standards.

2.3 Quantitative analysis is performed by GC/MS using extracted ion current profile (EICP) areas. Isotope dilution is used when labeled compounds are available; otherwise, an internal or external standard method is used.

2.4 Quality is assured through reproducible calibration and testing of the extraction and GC/MS systems.

3 Contamination and interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines causing misinterpretation of chromatograms and spectra. All materials shall be demonstrated to be free from interferences under the

conditions of analysis by running method blanks initially and with each sample lot (samples started through the extraction process on a given 8 hr shift, to a maximum of 20). Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Glassware and, where possible, reagents are cleaned by solvent rinse and baking at 450 °C for one hour minimum.

3.2 Interferences coextracted from samples will vary considerably from source to source, depending on the diversity of the industrial complex or municipality being samples.

4 Safety

4.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of data handling sheets should also be made available to all personnel involved in these analyses. Additional information on laboratory safety can be found in references 2-4.

4.2 The following compounds covered by this method have been tentatively classified as known or suspected human or mammalian carcinogens: benzo(a)anthracene, 3,3'-dichlorobenzidine, benzo(a)pyrene, dibenzo(a,h)anthracene, N-nitrosodimethylamine, and B-naphthylamine. Primary standards of these compounds shall be prepared in a hood, and a NIOSH/MESA approved toxic gas respirator should be worn when high concentrations are handled.

5 Apparatus and materials

5.1 Sampling equipment for discrete or composite sampling.

5.1.1 Sample bottle, amber glass, 1.1 liters minimum. If amber bottles are not available, samples shall be protected from light. Bottles are detergent water washed, then solvent rinsed or baked at 450 °C for one hour minimum before use.

5.1.2 Bottle caps—threaded to fit sample bottles. Caps are lined with Teflon. Aluminum foil may be substituted if the sample is not corrosive. Liners are detergent water washed, then reagent water (section 6.5) and solvent rinsed, and baked at approximately 200 °C for one hour minimum before use.

5.1.3 Compositing equipment—automatic or manual compositing system incorporating glass containers for collection of a minimum 1.1 liters. Sample containers are kept at 0 to 4 °C during sampling. Glass or Teflon tubing only shall be used. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used in the pump only. Before use, the tubing is thoroughly rinsed with methanol, followed by repeated rinsings with reagent water (section 6.5) to minimize sample contamination. An integrating flow meter is used to collect proportional composite samples.

5.2 Continuous liquid-liquid extractor—Teflon or glass connecting joints and stopcocks without lubrication (Hershberg-Wolf Extractor) one liter capacity, Ace Glass 6841-10, or equivalent.

5.3 Drying column—15 to 20 mm i.d. Pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

5.4 Kuderna-Danish (K-D) apparatus
5.4.1 Concentrator tube—10mL, graduated (Kontes K-570050-1025, or equivalent) with calibration verified. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

5.4.2 Evaporation flask—500 mL (Kontes K-570001-0500, or equivalent), attached to concentrator tube with springs (Kontes K-662750-0012).

5.4.3 Snyder column—three ball macro (Kontes K-503000-0232, or equivalent).

5.4.4 Snyder column—two ball micro (Kontes K-469002-0219, or equivalent).

5.4.5 Boiling chips—approx 10/40 mesh, extracted with methylene chloride and baked at 450 °C for one hr minimum.

5.5 Water bath—heated, with concentric ring cover, capable of temperature control (q 2 °C), installed in a fume hood.

5.6 Sample vials—amber glass, 2-5 mL with Teflon-lined screw cap.

5.7 Analytical balance—capable of weighing 0.1 mg.

5.8 Gas chromatograph—shall have splitless or on-column injection port for capillary column, temperature program with 30 °C hold, and shall meet all of the performance specifications in section 12.

5.8.1 Column—30±5 m×0.25±0.02 mm i.d. 5% phenyl, 94% methyl, 1% vinyl silicone bonded phase fused silica capillary column (J & W DB-5, or equivalent).

5.9 Mass spectrometer—70 eV electron impact ionization, shall repetitively scan from 35 to 450 amu in 0.95 to 1.00 second, and shall produce a unit resolution (valleys between m/z 441-442 less than 10 percent of the height of the 441 peak), background corrected mass spectrum from 50 ng decafluorotriphenylphosphine (DFTPP) introduced through the GC inlet. The spectrum shall meet the mass-intensity criteria in table 5 (reference 5). The mass spectrometer shall be interfaced to the GC such that the end of the capillary column terminates within one centimeter of the ion source but does not intercept the electron or ion beams. All portions of the column which connect the GC to the ion source shall remain at or above the column temperature during analysis to preclude condensation of less volatile compounds.

5.10 Data system—shall collect and record MS data, store mass-intensity data in spectral libraries, process GC/MS data, generate reports, and shall compute and record response factors.

5.10.1 Data acquisition—mass spectra shall be collected continuously throughout the analysis and stored on a mass storage device.

5.10.2 Mass spectral libraries—user created libraries containing mass spectra obtained from analysis of authentic standards shall be employed to reverse

search GC/MS runs for the compounds of interest (section 7.2).

5.10.3 Data processing—the data system shall be used to search, locate, identify, and quantify the compounds of interest in each GC/MS analysis. Software routines shall be employed to compute retention times and peak areas. Displays of spectra, mass chromatograms, and library comparisons are required to verify results.

5.10.4 Response factors and multipoint calibrations—the data system shall be used to record and maintain lists of response factors (response ratios for isotope dilution) and multipoint calibration curves (section 7). Computations of relative standard deviation (coefficient of variation) are useful for testing calibration linearity. Statistics on initial (section 8.2) and on-going (section 12.7) performance shall be computed and maintained.

6 Reagents and standards

6.1 Sodium hydroxide—reagent grade, 6N in reagent water.

6.2 Sulfuric acid—reagent grade, 6N in reagent water.

6.3 Sodium sulfate—reagent grade, granular anhydrous, rinsed with methylene chloride (20 mL/g) and conditioned at 450 °C for one hour minimum.

6.4 Methylene chloride—distilled in glass (Burdick and Jackson, or equivalent).

6.5 Reagent water—water in which the compounds of interest and interfering compounds are not detected by this method.

6.6 Standard solutions—purchased as solutions or mixtures with certification to their purity, concentration, and authenticity, or prepared from materials of known purity and composition. If compound purity is 96 percent or greater, the weight may be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at -20 to -10 °C in screw-capped vials with Teflon-lined lids. A mark is placed on the vial at the level of the solution so that solvent evaporation loss can be detected. The vials are brought to room temperature prior to use. Any precipitate is redissolved and solvent is added if solvent loss has occurred.

6.7 Preparation of stock solutions—prepare in methylene chloride, benzene, p-dioxane, or a mixture of these solvents per the steps below. Observe the safety precautions in section 4. The large number of labeled and unlabeled acid, base/neutral, and Appendix C compounds used for combined calibration (section 7) and calibration verification (12.5) require high concentrations (approx 40 mg/mL) when individual stock solutions are prepared, so that dilutions of mixtures will permit calibration with all compounds in a single set of solutions. The working range for most compounds is 10–200 µg/mL. Compounds with a reduced MS response may be prepared at higher concentrations.

6.7.1 Dissolve an appropriate amount of assayed reference material in a suitable solvent. For example, weigh 400 mg naphthalene in a 10 mL ground glass stoppered volumetric flask and fill to the mark with benzene. After the naphthalene is completely dissolved, transfer the solution to a 15 mL vial with Teflon-lined cap.

6.7.2 Stock standard solutions should be checked for signs of degradation prior to the preparation of calibration or performance test standards. Quality control check samples that can be used to determine the accuracy of calibration standards are available from the US Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6.7.3 Stock standard solutions shall be replaced after six months, or sooner if comparison with quality control check samples indicates a change in concentration.

6.8 Labeled compound spiking solution—from stock standard solutions prepared as above, or from mixtures, prepare the spiking solution at a concentration of 200 µg/mL, or at a concentration appropriate to the MS response of each compound.

6.9 Secondary standard—using stock solutions (section 6.7), prepare a secondary standard containing all of the compounds in tables 1 and 2 at a concentration of 400 µg/mL, or higher concentration appropriate to the MS response of the compound.

6.10 Internal standard solution—prepare 2,2'-difluorobiphenyl (DFB) at a concentration of 10 mg/mL in benzene.

6.11 DFTPP solution—prepare at 50 µg/mL in acetone.

6.12 Solutions for obtaining authentic mass spectra (section 7.2)—prepare mixtures of compounds at concentrations which will assure authentic spectra are obtained for storage in libraries.

6.13 Calibration solutions—combine 0.5 mL of the solution in section 6.8 with 25, 50, 125, 250, and 500 µL of the solution in section 6.9 and bring to 1.00 µL total volume each. This will produce calibration solutions of nominal 10, 20, 50, 100, and 200 µg/mL of the pollutants and a constant nominal 100 µg/mL of the labeled compounds. Spike each solution with 10 µL of the internal standard solution (section 6.10). These solutions permit the relative response (labeled to unlabeled) to be measured as a function of concentration (section 7.4).

6.14 Precision and recovery standard—used for determination of initial (section 8.2) and on-going (section 12.7) precision and recovery. This solution shall contain the pollutants and labeled compounds at a nominal concentration of 100 µg/mL.

6.15 Stability of solutions—all standard solutions (sections 6.8–6.14) shall be analyzed within 48 hours of preparation and on a monthly basis thereafter for signs of degradation. Standards will remain acceptable if the peak area at the quantitation mass relative to the DFB internal standard remains within ±15 percent of the area obtained in the initial analysis of the standard.

7 Calibration

7.1 Assemble the GC/MS and establish the operating conditions in table 3. Analyze standards per the procedure in section 11 to demonstrate that the analytical system meets the detection limits in tables 3 and 4, and the mass-intensity criteria in table 5 for 50 ng DFTPP.

7.2 Mass spectral libraries—detection and identification of compounds of interest are dependent upon spectra stored in user created libraries.

7.2.1 Obtain a mass spectrum of each pollutant, labeled compound, and the internal standard by analyzing an authentic standard either singly or as part of a mixture in which there is no interference between closely eluted components. That only a single compound is present is determined by examination of the spectrum. Fragments not attributable to the compound under study indicate the presence of an interfering compound.

7.2.2 Adjust the analytical conditions and scan rate (for this test only) to produce an undistorted spectrum at the GC peak maximum. An undistorted spectrum will usually be obtained if five complete spectra are collected across the upper half of the GC peak. Software algorithms designed to "enhance" the spectrum may eliminate distortion, but may also eliminate authentic masses or introduce other distortion.

7.2.3 The authentic reference spectrum is obtained under DFTPP tuning conditions (section 7.1 and table 5) to normalize it to spectra from other instruments.

7.2.4 The spectrum is edited by saving the 5 most intense mass spectral peaks and all other mass spectral peaks greater than 10 percent of the base peak. This edited spectrum is stored for reverse search and for compound confirmation.

7.3 Analytical range—demonstrate that 20 ng anthracene or phenanthrene produces an area at m/z 178 approx one-tenth that required to exceed the linear range of the system. The exact value must be determined by experience for each instrument. It is used to match the calibration range of the instrument to the analytical range and detection limits required, and to diagnose instrument sensitivity problems (section 15.4). The 20 µg/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.3.1 Polar compound detection—demonstrate that unlabeled pentachlorophenol and benzinidine are detectable at the 50 µg/mL level (per all criteria in section 13). The 50 µg/mL calibration standard (section 6.13) can be used to demonstrate this performance.

7.4 Calibration with isotope dilution—isotope dilution is used when 1) labeled compounds are available, 2) interferences do not preclude its use, and 3) the quantitation mass extracted ion current profile (EICP) area for the compound is in the calibration range. If any of these conditions preclude isotope dilution, internal or external standard methods (section 7.5 or 7.6) are used.

7.4.1 A calibration curve encompassing the concentration range is prepared for each compound to be determined. The relative response (pollutant to labeled) vs concentration in standard solutions is plotted or computed using a linear regression. The example in Figure 1 shows a calibration curve for phenol using phenol-d5 as the isotopic diluent. Also shown are the ± 10 percent error limits (dotted lines). Relative Response (RR) is determined according to the procedures described below. A minimum of five data points are employed for calibration.

7.4.2 The relative response of a pollutant to its labeled analog is determined from

isotope ratio values computed from acquired data. Three isotope ratios are used in this process:

R_x = the isotope ratio measured for the pure pollutant.

R_y = the isotope ratio measured for the labeled compound.

R_m = the isotope ratio of an analytical mixture of pollutant and labeled compounds.

The m/z 's are selected such that $R_x = R_y$. If R_m is not between $2R_y$ and $0.5R_x$, the method does not apply and the sample is analyzed by internal or external standard methods.

7.4.3 Capillary columns usually separate the pollutant-labeled pair, with the labeled compound eluted first (figure 2). For this case, R_x = [area m_1/z]/1, at the retention time of the pollutant (RT_1). R_y = 1/[area m_2/z], at the retention time of the labeled compound (RT_2). R_m = [area at m_1/z at RT_2]/[area at RT_1], as measured in the mixture of the pollutant and labeled compounds (figure 2), and $RR = R_m$.

7.4.4 Special precautions are taken when the pollutant-labeled pair is not separated, or when another labeled compound with interfering spectral masses overlaps the pollutant (a case which can occur with isomeric compounds). In this case, it is necessary to determine the respective contributions of the pollutant and labeled compounds to the respective EICP areas. If the peaks are separated well enough to permit the data system or operator to remove the contributions of the compounds to each other, the equations in section 7.4.3 apply. This usually occurs when the height of the valley between the two GC peaks at the same m/z is less than 10 percent of the height of the shorter of the two peaks. If significant GC and spectral overlap occur, RR is computed using the following equation: $RR = (R_y - R_m) / (R_x + 1) / (R_m - R_y + 1)$, where R_x is measured as shown in figure 3A, R_y is measured as shown in figure 3B, and R_m is measured as shown in figure 3C. For example, $R_x = 46100/4780 = 9.644$, $R_y = 2650/43600 = 0.0608$, $R_m = 49200/48300 = 1.019$, and $RR = 1.114$.

7.4.5 To calibrate the analytical system by isotope dilution, analyze a 1.0 μ L aliquot of each of the calibration standards (section 6.13) using the procedure in section 11. Compute the RR at each concentration.

7.4.6 Linearity—if the ratio of relative response to concentration for any compound is constant (less than 20 percent coefficient of variation) over the 5 point calibration range, and averaged relative response/concentration ratio may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point calibration range.

7.5 Calibration by internal standard—used when criteria for isotope dilution (section 7.4) cannot be met. The internal standard to be used for both acid and base/neutral analyses is 2,2'-difluorobiphenyl. The internal standard method is also applied to determination of compounds having no labeled analog, and to measurement of labeled compounds for intra-laboratory statistics (sections 8.4 and 12.7.4).

7.5.1 Response factors—calibration requires the determination of response factors (RF) which are defined by the following equation:

$RF = (A_x \times C_{is}) / (A_{is} \times C_x)$, where A_x is the area of the characteristic mass for the compound in the daily standard A_{is} is the area of the characteristic mass for the internal standard C_{is} is the concentration of the internal standard (μ g/mL) C_x is the concentration of the compound in the daily standard (μ g/mL)

7.5.1.1 The response factor is determined for at least five concentrations appropriate to the response of each compound (section 6.13); nominally, 10, 20, 50, 100, and 200 μ g/mL. The amount of internal standard added to each extract is the same (100 μ g/mL) so that C_{is} remains constant. The RF is plotted vs concentration for each compound in the standard (C_x) to produce a calibration curve.

7.5.1.2 Linearity—if the response factor (RF) for any compound is constant (less than 35 percent coefficient of variation) over the 5 point calibration range, an averaged response factor may be used for that compound; otherwise, the complete calibration curve for that compound shall be used over the 5 point range.

7.6 Combined calibration—by using calibration solutions (section 6.13) containing the pollutants, labeled compounds, and the internal standard, a single set of analyses can be used to produce calibration curves for the isotope dilution and internal standard methods. These curves are verified each shift (section 12.5) by analyzing the 100 μ g/mL calibration standard (section 6.13). Recalibration is required only if calibration verification (section 12.5) criteria cannot be met.

8 Quality assurance/quality control

8.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with labeled compounds to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in section 8.2.

8.1.2 The analyst is permitted to modify this method to improve separations or lower the costs of measurements, provided all performance specifications are met. Each time a modification is made to the method, the analyst is required to repeat the procedure in section 8.2 to demonstrate method performance.

8.1.3 Analyses of blanks are required to demonstrate freedom from contamination. The procedures and criteria for analysis of a blank are described in section 8.5.

8.1.4 The laboratory shall spike all samples with labeled compounds to monitor method performance. This test is described in section 8.3. When results of these spikes indicate atypical method performance for samples, the samples are diluted to bring

method performance within acceptable limits (section 15).

8.1.5 The laboratory shall, on an on-going basis, demonstrate through calibration verification and the analysis of the precision and recovery standard (section 6.14) that the analysis system is in control. These procedures are described in sections 12.1, 12.5, and 12.7.

8.1.6 The laboratory shall maintain records to define the quality of data that is generated. Development of accuracy statements is described in section 8.4.

8.2 Initial precision and accuracy—to establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

8.2.1 Extract, concentrate, and analyze two sets of four one-liter aliquots (8 aliquots total) of the precision and recovery standard (section 6.14) according to the procedure in section 10.

8.2.2 Using results of the first set of four analyses, compute the average recovery ($\bar{X}$) in μ g/mL and the standard deviation of the recovery (s) in μ g/mL for each compound, by isotope dilution for pollutants with a labeled analog, and by internal standard for labeled compounds and pollutants with no labeled analog.

8.2.3 For each compound, compare s and $\bar{X}$ with the corresponding limits for initial precision and accuracy in table 8. If s and $\bar{X}$ for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual $\bar{X}$ falls outside the range for accuracy, system performance is unacceptable for that compound. Note: The large number of compounds in table 8 present a substantial probability that one or more will fail the acceptance criteria when all compounds are analyzed. To determine if the analytical system is out of control, or if the failure can be attributed to probability, proceed as follows:

8.2.4 Using the results of the second set of four analyses, compute s and $\bar{X}$ for only those compounds which failed the test of the first set of four analyses (section 8.2.3). If these compounds now pass, system performance is acceptable for all compounds and analysis of blanks and samples may begin. If, however, any of the same compounds fail again, the analysis system is not performing properly for these compounds. In this event, correct the problem and repeat the entire test (section 8.2.1).

8.3 The laboratory shall spike all samples with labeled compounds to assess method performance on the sample matrix.

8.3.1 Analyze each sample according to the method in section 10.

8.3.2 Compute the percent recovery (P) of the labeled compounds using the internal standard method (section 7.5).

8.3.3 Compare the labeled compound recovery for each compound with the corresponding limits in table 8. If the recovery of any compounds falls outside its warning limit, method performance is unacceptable for that compound in that sample. Therefore, the sample is complex and

is to be diluted and reanalyzed per section 15.4.

8.4 As part of the QA program for the laboratory, method accuracy for wastewater samples shall be assessed and records shall be maintained. After the analysis of five wastewater samples for which the labeled compounds pass the tests in section 8.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (s_p) for the labeled compounds only. Express the accuracy assessment as a percent recovery interval from $P - 2s_p$ to $P + 2s_p$. For example, if $P = 90\%$ and $s_p = 10\%$, the accuracy interval is expressed as 70–100%. Update the accuracy assessment for each compound on a regular basis (e.g. after each 5–10 new accuracy measurements).

8.5 Blanks—reagent water blanks are analyzed to demonstrate freedom from contamination.

8.5.1 Extract and concentrate a blank with each sample lot (samples started through the extraction process on the same 8 hr shift, to a maximum of 20 samples). Analyze the blank immediately after analysis of the precision and recovery standard (section 6.14) to demonstrate freedom from contamination.

8.5.2 If any of the compounds of interest (tables 1 and 2) or any potentially interfering compound is found in a blank at greater than 10 $\mu\text{g/L}$ (assuming a response factor of 1 relative to the internal standard for compounds not listed in tables 1 and 2), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination at this level.

8.6 The specifications contained in this method can be met if the apparatus used is calibrated properly, then maintained in a calibrated state. The standards used for calibration (section 7), calibration verification (section 12.5), and for initial (section 8.2) and on-going (section 12.7) precision and recovery should be identical, so that the most precise results will be obtained. The GC/MS instrument in particular will provide the most reproducible results if dedicated to the settings and conditions required for the analysis of semi-volatiles by this method.

8.7 Depending on specific program requirements, field replicates may be collected to determine the precision of the sampling technique, and spiked samples may be required to determine the accuracy of the analysis when internal or external standard methods are used.

9 Sample collection, preservation, and handling

9.1 Collect samples in glass containers following conventional sampling practices (reference 7). Composite samples are collected in refrigerated glass containers (section 5.1.3) in accordance with the requirements of the sampling program.

9.2 Maintain samples at 0–4 °C from the time collection until extraction. If residual chlorine is present, add 80 mg sodium thiosulfate per liter of water. EPA methods 330.4 and 330.5 may be used to measure residual chlorine (reference 8).

9.3 Begin sample extraction within seven days of collection, and analyze all extracts within 40 days of extraction.

10 Sample extraction and concentration (See figure 4)

10.1 Labeled compound spiking—measure 1.00 $\pm$ 0.01 liter of sample into a glass container. For untreated effluents, and samples which are expected to be difficult to extract and/or concentrate, measure an additional 10.0 $\pm$ 0.1 mL and dilute to a final volume of 1.00 $\pm$ 0.01 liter with reagent water in a glass container.

10.1.1 For each sample or sample lot (to a maximum of 20) to be extracted at the same time, place three 1.00 $\pm$ 0.10 liter aliquots of reagent water in glass containers.

10.1.2 Spike 0.5 mL of the labeled compound spiking solution (section 6.8) into all samples and one reagent water aliquot.

10.1.3 Spike 1.0 mL of the precision and recovery standard (section 6.14) into the two remaining reagent water aliquots.

10.1.4 Stir and equilibrate all solutions for 1–2 hr.

10.2 Base/neutral extraction—place 100–150 mL methylene chloride in each continuous extractor and 200–300 mL in each distilling flask.

10.2.1 Pour the sample(s), blank, and standard aliquots into the extractors. Rinse the glass containers with 50–100 mL methylene chloride and add to the respective extractor.

10.2.2 Adjust the pH of the waters in the extractors to 12–13 with 6N NaOH while monitoring with a pH meter. Begin the extraction by heating the flask until the methylene chloride is boiling. When properly adjusted, 1–2 drops of methylene chloride per second will fall from the condenser tip into the water. After 1–2 hours of extraction, test the pH and readjust to 12–13 if required. Extract for 18–24 hours.

10.2.3 Remove the distilling flask, estimate and record the volume of extract (to the nearest 100 mL), and pour the contents through a drying column containing 7 to 10 cm anhydrous sodium sulfate. Rinse the distilling flask with 30–50 mL of methylene chloride and pour through the drying column. Collect the solution in a 500 mL K-D evaporator flask equipped with a 10 mL concentrator tube. Seal, label as the base/neutral fraction, and concentrate per sections 10.4 to 10.5.

10.3 Acid extraction—adjust the pH of the waters in the extractors to 2 or less using 6N sulfuric acid. Charge clean distilling flasks with 300–400 mL of methylene chloride. Test and adjust the pH of the waters after the first 1–2 hr of extraction. Extract for 18–24 hours.

10.3.1 Repeat section 10.2.3, except label as the acid fraction.

10.4 Concentration—concentrate the extracts in separate 500 mL K-D flasks equipped with 10 mL concentrator tubes.

10.4.1 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro Snyder column. Prewet the column by adding approximately one mL of methylene chloride through the top. Place the K-D apparatus in a hot water bath so that the entire lower rounded surface of the flask is bathed with steam. Adjust the vertical position of the

apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid has reached an apparent volume of 1 mL, remove the K-D apparatus from the bath and allow the solvent to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 mL of methylene chloride. A 5-mL syringe is recommended for this operation.

10.4.2 For performance standards (sections 8.2 and 12.7) and for blanks (section 8.5), combine the acid and base/neutral extracts for each at this point. Do not combine the acid and base/neutral extracts for samples.

10.5 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approx 0.5 mL methylene chloride through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the liquid reaches an apparent volume of approx 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint into the concentrator tube with approx 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL.

10.6 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid, and mark the level on the vial. Label with the sample number and fraction, and store in the dark at –20 to –10 °C until ready for analysis.

11 GC/MS analysis

11.1 Establish the operating conditions given in tables 3 or 4 for analysis of the base/neutral or acid extracts, respectively. For analysis of combined extracts (section 10.4.2), use the operating conditions in table 3.

11.2 Bring the concentrated extract (section 10.6) or standard (sections 6.13–6.14) to room temperature and verify that any precipitate has redissolved. Verify the level on the extract (sections 6.6 and 10.6) and bring to the mark with solvent if required.

11.3 Add the internal standard solution (section 6.10) to the extract (use 1.0 μL of solution per 0.1 mL of extract) immediately prior to injection to minimize the possibility of loss by evaporation, adsorption, or reaction. Mix thoroughly.

11.4 Inject a volume of the standard solution or extract such that 100 ng of the internal standard will be injected, using on-column or splitless injection. For 1 mL extracts, this volume will be 1.0 μL . Start the GC column initial isothermal hold upon injection. Start MS data collection after the solvent peak elutes. Stop data collection after the benzo (ghi) perylene or pentachlorophenol peak elutes for the base/neutral or acid fraction, respectively. Return

the column to the initial temperature for analysis of the next sample.

12 System and laboratory performance

12.1 At the beginning of each 8 hr shift during which analyses are performed, GC/MS system performance and calibration are verified for all pollutants and labeled compounds. For these test, analysis of the 100 µg/mL calibration standard (section 6.13) shall be used to verify all performance criteria. Adjustment and/or recalibration (per section 7) shall be performed until all performance criteria are met. Only after all performance criteria are met may samples, blanks, and precision and recovery standards be analyzed.

12.2 DFTPP spectrum validity—inject 1 µL of the DFTPP solution (section 6.11) either separately or within a few seconds of injection of the standard (section 12.1) analyzed at the beginning of each shift. The criteria in table 5 shall be met.

12.3 Retention times—the absolute retention time of 2,2'-difluorobiphenyl shall be within the range of 1078 to 1248 seconds and the relative retention times of all pollutants and labeled compounds shall fall within the limits given in tables 3 and 4.

12.4 GC resolution—the valley height between anthracene and phenanthrene at m/z 178 (or the analogs at m/z 188) shall not exceed 10 percent of the taller of the two peaks.

12.5 Calibration verification—compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method. These concentrations are computed based on the calibration data determined in section 7.

12.5.1 For each pollutant and labeled compound being tested, compare the concentration with the calibration verification limit in table 8. If all compounds meet the acceptance criteria, calibration has been verified and analysis of blanks, samples, and precision and recovery standards may proceed. If, however, any compound fails, the measurement system is not performing properly for that compound. In this event, prepare a fresh calibration standard or correct the problem causing the failure and repeat the test (section 12.1), or recalibrate (section 7).

12.6 Multiple peaks—each compound injected shall give a single, distinct GC peak.

12.7 On-going precision and accuracy.

12.7.1 Analyze the extract of one of the pair of precision and recovery standards (section 10.1.3) prior to analysis of samples from the same lot.

12.7.2 Compute the concentration of each pollutant (tables 1 and 2) by isotope dilution (section 7.4) for those compounds which have labeled analogs. Compute the concentration of each pollutant which has no labeled analog by the internal standard method (section 7.5). Compute the concentration of the labeled compounds by the internal standard method.

12.7.3 For each pollutant and labeled compound, compare the concentration with

the limits for on-going accuracy in table 8. If all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual concentration falls outside of the range given, system performance is unacceptable for that compound. NOTE: The large number of compounds in table 8 present a substantial probability that one or more will fail when all compounds are analyzed. To determine if the extraction/concentration system is out of control or if the failure is caused by probability, proceed as follows:

12.7.3.1 Analyze the second aliquot of the pair of precision and recovery standard (section 10.1.3).

12.7.3.2 Compute the concentration of only those pollutants or labeled compounds that failed the previous test (section 12.7.3). If these compounds now pass, the extraction/concentration processes are in control and analysis of blanks and samples may proceed. If, however, any of the same compounds fail again, the extraction/concentration processes are not being performed properly for these compounds. In this event, correct the problem, re-extract the sample lot (section 10) and repeat the on-going precision and recovery test (section 12.7).

12.7.4 Add results which pass the specifications in section 12.7.2 to initial and previous on-going data. Update QC charts to perform a graphic representation of continued laboratory performance (Figure 5). Develop a statement of laboratory accuracy for each pollutant and labeled compound by calculating the average percent recovery (R) and the standard deviation of percent recovery (s_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if $R = 95\%$ and $s_r = 5\%$, the accuracy is $85 - 105\%$.

13 Qualitative determination

13.1 Qualitative determination is accomplished by comparison of data from analysis of a sample or blank with data from analysis of the shift standard (section 12.1) and with data stored in the spectral libraries (section 7.2.4). Identification is confirmed when spectra and retention times agree per the criteria below.

13.2 Labeled compounds and pollutants having no labeled analog:

13.2.1 The signals for all characteristic masses stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.2.2 Either (1) the background corrected EICP areas, or (2) the corrected relative intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two (0.5 to 2 times) for all masses stored in the library.

13.2.3 The retention time relative to the nearest eluted internal standard shall be within ± 15 scans or ± 15 seconds, whichever is greater of this difference in the shift standard (section 12.1).

13.3 Pollutants having a labeled analog:

13.3.1 The signals for all characteristic masses stored in the spectral library (section 7.2.4) shall be present and shall maximize within the same two consecutive scans.

13.3.2 Either (1) the background corrected EICP areas, or (2) the corrected relative

intensities of the mass spectral peaks at the GC peak maximum shall agree within a factor of two for all masses stored in the spectral library.

13.3.3 The retention time difference between the pollutant and its labeled analog shall agree within ± 6 scans or ± 6 seconds (whichever is greater) of this difference in the shift standard (section 12.1).

13.4 Masses present in the experimental mass spectrum that are not present in the reference mass spectrum shall be accounted for by contaminant or background ions. If the experimental mass spectrum is contaminated, an experienced spectrometrist (section 1.4) is to determine the presence or absence of the compound.

14 Quantitative determination

14.1 Isotope dilution—by adding a known amount of a labeled compound to every sample prior to extraction, correction for recovery of the pollutant can be made because the pollutant and its labeled analog exhibit the same effects upon extraction, concentration, and gas chromatography. Relative response (RR) values for mixtures are used in conjunction with calibration curves described in section 7.4 to determine concentrations directly, so long as labeled compound spiking levels are constant. For the phenol example given in figure 1 (section 7.4.1), RR would be equal to 1.114. For this RR value, the phenol calibration curve given in figure 1 indicates a concentration of 27 µg/mL in the sample extract (C_{ex}).

14.2 Internal standard—compute the concentration in the extract using the response factor determined from calibration data (section 7.5) and the following equation: $C_{ex}(\mu\text{g/mL}) = (A_s \times C_{is}) / (A_{is} \times RF)$ where C_{ex} is the concentration of the compound in the extract, and the other terms are as defined in section 7.5.1.

14.3 The concentration of the pollutant in water is computed using the volumes of the original water sample (section 10.1) and the final extract volume (section 10.5), as follows: Concentration in water ($\mu\text{g/L}$) = $(C_{ex} \times V_{ex}) / V_s$ where V_{ex} is the extract volume in mL, and V_s is the sample volume in liters.

14.4 If the EICP area at the quantitation mass for any compound exceeds the calibration range of the system, the extract of the dilute aliquot (section 10.1) is analyzed by isotope dilution; otherwise, the extract is diluted by a factor of 10, 9 µL of internal standard solution (section 6.10) are added to a 1.0 mL aliquot, and this diluted extract is analyzed by the internal standard method (section 14.2). Quantify each compound at the highest concentration level within the calibration range.

14.5 Report results for all pollutants and labeled compounds (tables 1 and 2) found in all standards, blanks, and samples in µg/L, to three significant figures. Results for samples which have been diluted are reported at the least dilute level at which the area at the quantitation mass is within the calibration range (section 14.4) and the labeled compound recovery is within the normal range for the method (section 15.4).

15 Analysis of complex samples

15.1 Untreated effluents and other samples frequently contain high levels (>1000 µg/L) of the compounds of interest, interfering compounds, and/or polymeric materials. Some samples will not concentrate to one mL (section 10.5); others will overload the GC column and/or mass spectrometer.

15.2 Analyze the dilute aliquot (section 10.1) when the sample will not concentrate to 1.0 mL. If a dilute aliquot was not extracted, and the sample holding time (section 9.3) has not been exceeded, dilute an aliquot of the sample with reagent water and re-extract (section 10.1); otherwise, dilute the extract (section 14.4) and analyze by the internal standard method (section 14.2).

15.3 Recovery of internal standard—the EICP area of the internal standard should be within a factor of two of the area in the shift standard (section 12.1). If the absolute areas of the labeled compounds are within a factor of two of the respective areas in the shift standard, and the internal standard area is less than one-half of its respective area, then internal standard loss in the extract has occurred. In this case, use one of the labeled compounds (preferably a polynuclear aromatic hydrocarbon) to compute the concentration of a pollutant with no labeled analog.

15.4 Recovery of labeled compounds—in most samples, labeled compound recoveries will be similar to those from reagent water

(section 12.7). If the labeled compound recovery is outside the limits given in table 8, the dilute extract (section 10.1) is analyzed as in section 14.4. If the recoveries of all labeled compounds and the internal standard are low (per the criteria above), then a loss in instrument sensitivity is the most likely cause. In this case, the 100 µg/mL calibration standard (section 12.1) shall be analyzed and calibration verified (section 12.5). If a loss in sensitivity has occurred, the instrument shall be repaired, the performance specifications in section 12 shall be met, and the extract reanalyzed. If a loss in instrument sensitivity has not occurred, the method does not work on the sample being analyzed and the result may not be reported for regulatory compliance purposes.

16 Method performance

16.1 Interlaboratory performance for this method is detailed in references 9 and 10.

16.2 A chromatogram of the 100 µg/mL acid/base/neutral calibration standard (section 6.13) is shown in figure 6.

References

1. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories" USEPA, EMSL/Cincinnati, OH 45268, EPA-600/4-80-025 (April 1980).
2. "Working with Carcinogens," DHEW, PHS, CDC, NIOSH, Publication 77-206, (Aug 1977).

3. "OSHA Safety and Health Standards, General Industry" OSHA 2206, 29 CFR 1910 (Jan 1976).

4. "Safety in Academic Chemistry Laboratories," ACS Committee on Chemical Safety (1979).

5. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," J.W. Eichelberger, L.E. Harris, and W.L. Budde, Anal. Chem., 47, 955 (1975).

6. "Handbook of Analytical Quality Control in Water and Wastewater Laboratories," USEPA, EMSL/Cincinnati, OH 45268, EPA-600/4-79-019 (March 1979).

7. "Standard Practice for Sampling Water," ASTM Annual Book of Standards, ASTM, Philadelphia, PA, 76 (1980).

8. "Methods 330.4 and 330.5 for Total Residual Chlorine," USEPA, EMSL/Cincinnati, OH 45268, EPA 600/4-70-020 (March 1979).

9. Colby, B.N., Beimer, R.G., Rushneck, D.R., and Telliard, W.A., "Isotope Dilution Gas Chromatography-Mass Spectrometry for the determination of Priority Pollutants in Industrial Effluents," USEPA, Effluent Guidelines Division, Washington, DC 20460 (1980).

10. "Inter-laboratory Validation of US Environmental Protection Agency Method 1625," USEPA, Effluent Guidelines Division, Washington, DC 20460 (June 15, 1984).

TABLE 1.—Base/Neutral Extractable Compounds

Compound	Storet	CAS registry	EPA-EGD	NPDES
Acenaphthene	34205	83-32-9	001 B	001 B
Acenaphthylene	34200	208-96-8	077 B	002 B
Anthracene	34220	120-12-7	078 B	003 B
Benzidine	39120	92-87-5	005 B	004 B
Benzo(a)anthracene	34526	56-55-3	072 B	005 B
Benzo(b)fluoranthene	34230	205-99-2	074 B	007 B
Benzo(k)fluoranthene	34242	207-08-9	075 B	009 B
Benzo(a)pyrene	34247	50-32-8	073 B	006 B
Benzo(ghi)perylene	34521	191-24-2	079 B	008 B
Biphenyl (Appendix C)	81513	92-52-4	512 B	
Bis(2-chloroethyl) ether	34273	111-44-4	018 B	011 B
Bis(2-chloroethoxy)methane	34278	111-91-1	043 B	010 B
Bis(2-chloroisopropyl) ether	34283	108-60-1	042 B	012 B
Bis(2-ethylhexyl) phthalate	39100	117-81-7	066 B	013 B
4-bromophenyl phenyl ether	34636	101-55-3	041 B	014 B
Butyl benzyl phthalate	34292	85-68-7	067 B	015 B
n-C10 (Appendix C)	77427	124-18-5	517 B	
n-C12 (Appendix C)	77598	112-40-2	506 B	
n-C14 (Appendix C)	77691	629-59-4	518 B	
n-C16 (Appendix C)	77757	544-76-3	519 B	
n-C18 (Appendix C)	77804	593-45-3	520 B	
n-C20 (Appendix C)	77830	112-95-8	521 B	
n-C22 (Appendix C)	77859	629-97-0	522 B	
n-C24 (Appendix C)	77886	646-31-1	523 B	
n-C26 (Appendix C)	77901	630-01-3	524 B	
n-C28 (Appendix C)	78116	630-02-4	525 B	
n-C30 (Appendix C)	78117	638-68-6	526 B	
Carbazole (4c)	77571	86-74-8	528 B	
2-chloronaphthalene	34581	91-58-7	020 B	016 B
4-chlorophenyl phenyl ether	34641	7005-72-3	040 B	017 B
Chrysene	34320	218-01-9	076 B	018 B
p-cymene (Appendix C)	77358	99-87-6	513 B	
Dibenzo(a,h)anthracene	34556	53-70-3	082 B	019 B
Dibenzofuran (Appendix C and 4c)	81302	132-64-9	505 B	
Dibenzothiophene (Synfuel)	77639	132-65-0	504 B	
Di-n-butyl phthalate	39110	84-74-2	068 B	026 B
1,2-dichlorobenzene	34536	95-50-1	025 B	020 B
1,3-dichlorobenzene	34566	541-73-1	026 B	021 B
1,4-dichlorobenzene	34571	106-46-7	027 B	022 B
3,3'-dichlorobenzidine	34631	91-94-1	028 B	023 B
Diethyl phthalate	34336	84-68-2	070 B	024 B
2,4-dimethylphenol	34606	105-67-9	034 A	003 A
Dimethyl phthalate	34341	131-11-3	071 B	025 B
2,4-dinitrotoluene	34611	121-14-2	035 B	027 B
2,6-dinitrotoluene	34626	606-20-2	036 B	028 B
Di-n-octyl phthalate	34596	117-84-0	069 B	029 B

TABLE 1.—Base/Neutral Extractable Compounds—Continued

Compound	Storet	CAS registry	EPA-EGD	NPDES
Diphenylamine (Appendix C)	77579	122-39-4	507 B	
Diphenyl ether (Appendix C)	77587	101-84-8	508 B	
1,2-diphenylhydrazine	34346	122-86-7	037 B	030 B
Fluoranthene	34376	206-44-0	039 B	031 B
Fluorene	34381	86-73-7	080 B	032 B
Hexachlorobenzene	39700	118-74-1	009 B	033 B
Hexachlorobutadiene	34391	87-68-3	052 B	034 B
Hexachloroethane	34396	67-72-1	012 B	036 B
Hexachlorocyclopentadiene	34386	77-47-4	053 B	035 B
Indeno(1,2,3-cd)pyrene	34403	193-39-5	083 B	037 B
Isophorone	34408	78-59-1	054 B	038 B
Naphthalene	34696	91-20-3	055 B	039 B
B-naphthylamine (Appendix C)	82553	91-59-8	502 B	
Nitrobenzene	34447	98-95-3	056 B	040 B
N-nitrosodimethylamine	34438	62-75-9	061 B	041 B
N-nitrosodi-n-propylamine	34428	621-64-7	063 B	042 B
N-nitrosodiphenylamine	34433	86-30-3	062 B	043 B
Phenanthrene	34461	85-01-8	081 B	044 B
Phenol	34694	108-95-2	085 A	010 A
a-picoline (Synfuel)	77088	109-06-89	503 B	
Pyrene	34469	129-00-0	084 B	045 B
styrene (Appendix C)	77128	100-42-5	510 B	
a-terpineol (Appendix C)	77493	98-55-5	509 B	
1,2,3-trichlorobenzene (4c)	77613	87-61-6	529 B	
1,2,4-trichlorobenzene	34551	120-82-1	008 B	046 B

TABLE 2.—Acid Extractable Compounds

Compound	Storet	CAS registry	EPA-EGD	NPDES
4-chloro-3-methylphenol	34452	59-50-7	022 A	008 A
2-chlorophenol	34586	95-57-8	024 A	001 A
2,4-dichlorophenol	34601	120-83-2	031 A	002 A
2,4-dinitrophenol	34616	51-28-5	059 A	005 A
2-methyl-4,6-dinitrophenol	34657	534-52-1	060 A	004 A
2-nitrophenol	34591	88-75-5	057 A	006 A
4-nitrophenol	34646	100-02-7	058 A	007 A
Pentachlorophenol	39032	87-86-5	064 A	009 A
2,3,6-trichlorophenol (4c)	77688	93-37-55	530 A	
2,4,5-trichlorophenol (4c)		95-95-4	531 A	
2,4,6-trichlorophenol	34621	88-06-2	021 A	011 A

TABLE 3.—GAS CHROMATOGRAPHY OF BASE/NEUTRAL EXTRACTABLE COMPOUNDS

EGD No. 1	Compound	Retention time			Detection limit $\pm$ (μ g/L)
		Mean (sec)	EGD Ref	Relative	
164	2,2'-difluorobiphenyl (int std)	1163	164	1.000-1.000	10
061	N-nitrosodimethylamine	385	164	ns	50
603	alpha picoline-d7	417	164	0.326-0.393	50
703	alpha picoline	426	603	1.006-1.028	50
610	styrene-d5	546	164	0.450-0.488	10
710	styrene	549	610	1.002-1.009	10
613	p-cymene-d14	742	164	0.624-0.652	10
713	p-cymene	755	613	1.008-1.023	10
265	phenol-d5	696	164	0.584-0.613	10
365	phenol	700	265	0.995-1.010	10
218	bis(2-chloroethyl) ether-d8	696	164	0.584-0.607	10
318	bis(2-chloroethyl) ether	704	218	1.007-1.016	10
617	n-decane-d22	698	164	0.585-0.615	10
717	n-decane	720	617	1.022-1.038	10
226	1,3-dichlorobenzene-d4	722	164	0.605-0.636	10
326	1,3-dichlorobenzene	724	226	0.998-1.008	10
227	1,4-dichlorobenzene-d4	737	164	0.601-0.666	10
327	1,4-dichlorobenzene	740	227	0.997-1.009	10
225	1,2-dichlorobenzene-d4	758	164	0.632-0.667	10
325	1,2-dichlorobenzene	760	225	0.995-1.008	10
242	bis(2-chloroisopropyl) ether-d12	768	164	0.664-0.691	10
342	bis(2-chloroisopropyl) ether	799	242	1.010-1.016	10
212	hexachloroethane-13C	819	164	0.690-0.717	10
312	hexachloroethane	823	212	0.999-1.001	10
063	N-nitrosodi-n-propylamine	830	164	ns	20
256	nitrobenzene-d5	845	164	0.706-0.727	10
356	nitrobenzene	849	256	1.002-1.007	10
254	isophorone-d8	881	164	0.747-0.767	10
354	isophorone	889	254	0.999-1.017	10
234	2,4-dimethylphenol	921	164	0.781-0.803	10
334	2,4-dimethylphenol	924	234	0.999-1.003	10
043	bis(2-chloroethoxy) methane	939	164	ns	10
208	1,2,4-trichlorobenzene-d3	955	164	0.813-0.830	10
308	1,2,4-trichlorobenzene	958	208	1.000-1.005	10
255	naphthalene-d8	963	164	0.819-0.836	10
355	naphthalene	967	255	1.001-1.006	10
609	alpha-terpineol-d3	973	164	0.829-0.844	10
709	alpha-terpineol	975	609	0.998-1.008	10
606	n-dodecane-d26	953	164	0.730-0.908	10
706	n-dodecane	981	606	0.986-1.051	10

TABLE 3.—GAS CHROMATOGRAPHY OF BASE/NEUTRAL EXTRACTABLE COMPOUNDS—Continued

EGD No. ¹	Compound	Retention time			Detection limit ² (μg/L)
		Mean (sec)	EGD Ref	Relative	
529	1,2,3-trichlorobenzene	1003	164	ns	10
252	hexachlorobutadiene-13C4	1005	164	0.856-0.871	10
352	hexachlorobutadiene	1006	252	0.999-1.002	10
253	hexachlorocyclopentadiene-13C4	1147	164	0.976-0.986	10
353	hexachlorocyclopentadiene	1142	253	0.999-1.001	10
220	2-chloronaphthalene-d7	1185	164	1.014-1.024	10
320	2-chloronaphthalene	1200	220	0.997-1.007	10
518	n-tetradecane	1203	164	ns	10
612	Biphenyl-d10	1205	164	1.016-1.027	10
712	Biphenyl	1195	612	1.001-1.006	10
608	Diphenyl ether-d10	1211	164	1.036-1.047	10
708	Diphenyl ether	1216	608	0.997-1.009	10
277	Acenaphthylene-d8	1265	164	1.080-1.095	10
377	Acenaphthylene	1247	277	1.000-1.004	10
271	Dimethyl phthalate-d4	1269	164	1.083-1.102	10
371	Dimethyl phthalate	1273	271	0.998-1.005	10
236	2,6-dinitrotoluene-d3	1283	164	1.090-1.112	10
336	2,6-dinitrotoluene	1300	236	1.001-1.005	10
201	Acenaphthene-d10	1298	164	1.107-1.125	10
301	Acenaphthene	1304	201	0.999-1.009	10
605	Dibenzofuran-d8	1331	164	1.134-1.155	10
705	Dibenzofuran	1335	605	0.998-1.007	10
602	Beta-naphthylamine-d7	1368	164	1.163-1.189	50
702	Beta-naphthylamine	1371	602	0.996-1.007	50
280	Fluorene-d10	1395	164	1.185-1.214	10
380	Fluorene	1401	280	0.999-1.008	10
240	4-chlorophenyl phenyl ether-d5	1406	164	1.194-1.223	10
340	4-chlorophenyl phenyl ether	1409	240	0.990-1.015	10
270	Diethyl phthalate-d4	1409	164	1.197-1.229	10
370	Diethyl phthalate	1414	270	0.996-1.006	10
619	n-hexadecane-d34	1447	164	1.010-1.478	10
719	n-hexadecane	1469	619	1.013-1.020	10
235	2,4-dinitrotoluene-d3	1359	164	1.152-1.181	10
335	2,4-dinitrotoluene	1344	235	1.000-1.002	10
237	1,2-diphenylhydrazine-d8	1433	164	1.216-1.248	20
337	1,2-diphenylhydrazine (P)	1439	237	0.999-1.009	20
607	Diphenylamine-d10	1437	164	1.213-1.249	20
707	Diphenylamine	1439	607	1.000-1.007	20
262	N-nitrosodiphenylamine-d6	1447	164	1.225-1.252	20
362	N-nitrosodiphenylamine (S)	1464	262	1.000-1.002	20
041	4-bromophenyl phenyl ether	1498	164	1.271-1.307	10
209	Hexachlorobenzene-13C6	1521	164	1.288-1.327	10
309	Hexachlorobenzene	1522	209	0.999-1.001	10
281	Phenanthrene-d10	1578	164	1.334-1.380	10
520	n-octadecane	1580	164	ns	10
381	Phenanthrene	1583	281	1.000-1.005	10
278	Anthracene-d10	1588	164	1.342-1.388	10
378	Anthracene	1592	278	0.998-1.006	10
604	Dibenzothiophene-d8	1559	164	1.314-1.361	10
704	Dibenzothiophene	1564	604	1.000-1.006	10
528	Carbazole	1650	164	ns	20
621	n-eicosane-d42	1655	164	1.184-1.662	10
721	n-eicosane	1677	621	1.010-1.021	10
268	Di-n-butyl phthalate-d4	1719	164	1.446-1.510	10
368	Di-n-butyl phthalate	1723	268	1.000-1.003	10
239	Fluoranthene-d10	1813	164	1.522-1.596	10
339	Fluoranthene	1817	239	1.000-1.004	10
284	Pyrene-d10	1844	164	1.523-1.644	10
384	Pyrene	1852	284	1.001-1.003	10
205	Benzo(a)anthracene-d8	1854	164	1.549-1.632	50
305	Benzo(a)anthracene	1853	205	1.000-1.002	50
522	n-docosane	1889	164	ns	10
623	n-tetracosane-d50	1997	164	1.671-1.764	10
723	n-tetracosane	2025	612	1.012-1.015	10
067	Butylbenzyl phthalate	2060	164	ns	10
276	Chrysene-d12	2081	164	1.743-1.837	10
376	Chrysene	2083	276	1.000-1.004	10
272	Benzo(a)anthracene-d12	2082	164	1.735-1.846	10
372	Benzo(a)anthracene	2090	272	0.999-1.007	50
228	3,3'-dichlorobenzidine-d6	2088	164	1.744-1.848	50
328	3,3'-dichlorobenzidine	2086	228	1.000-1.001	50
266	Bis(2-ethylhexyl) phthalate-d4	2123	164	1.771-1.880	10
366	Bis(2-ethylhexyl) phthalate	2124	266	1.000-1.002	10
524	n-hexacosane	2147	164	ns	10
269	di-n-octyl phthalate-d4	2239	164	1.867-1.982	10
369	di-n-octyl phthalate	2240	269	1.000-1.002	10
525	n-octacosane	2272	164	ns	10
274	Benzo(b)fluoranthene-d12	2281	164	1.902-2.025	10
354	Benzo(b)fluoranthene	2293	274	1.000-1.005	10
275	Benzo(k)fluoranthene-d12	2287	164	1.908-2.033	10
375	Benzo(k)fluoranthene	2293	275	1.000-1.005	10
273	Benzo(a)pyrene-d12	2351	164	1.954-2.088	10
373	Benzo(a)pyrene	2350	273	1.000-1.004	10
626	N-triacontane-d62	2384	164	1.972-2.127	10
726	N-triacontane	2429	626	1.011-1.028	10
083	Indeno(1,2,3-cd)pyrene	2650	164	ns	20
082	Dibenzo(a,h)anthracene	2650	164	ns	20
279	Benzo(ghi)perylene-d12	2741	164	2.187-2.524	20
379	Benzo(ghi)perylene	2750	279	1.001-1.006	20

¹ Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

² This is a minimum level at which the entire GC/MS system must give recognizable mass spectra (background corrected) and accepted calibration points.

³ Detected as azobenzene.

⁴ Detected as diphenylamine.

ns = specification not available at time of release of method.

Column: 30 ± 2 m × 0.25 ± 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary.

Temperature program: 5 min at 30 °C; 30–280 °C at 8 °C per min; isothermal at 280 °C until benzo[ghi]perylene elutes.

Gas velocity: 30 ± 5 cm/sec.

TABLE 4.—GAS CHROMATOGRAPHY OF ACID EXTRACTABLE COMPOUNDS

EGD No. ¹	Compound	Retention time			Detection limit ² (µg/L)
		Mean (sec)	EGD Ref	Relative	
164	2,2'-difluorobiphenyl (ins std)	1163	164	1.000-1.000	10
224	2-chlorophenol-d4	701	164	0.587-0.618	10
324	2-chlorophenol	705	224	0.997-1.010	10
257	2-nitrophenol-d4	898	164	0.761-0.783	20
357	2-nitrophenol	900	257	0.994-1.009	20
231	2,4-dichlorophenol-d3	944	164	0.802-0.822	10
331	2,4-dichlorophenol	947	231	0.997-1.006	10
222	4-chloro-3-methylphenol-d2	1086	164	0.930-0.943	10
322	4-chloro-3-methylphenol	1091	222	0.998-1.003	10
221	2,4,6-trichlorophenol-d2	1162	164	0.994-1.005	10
321	2,4,6-trichlorophenol	1165	221	0.998-1.004	10
531	2,4,5-trichlorophenol	1170	164	ns	10
530	2,3,6-trichlorophenol	1195	164	ns	10
259	2,4-dinitrophenol-d3	1323	164	1.127-1.149	50
359	2,4-dinitrophenol	1325	259	1.000-1.005	50
258	4-nitrophenol-d4	1349	164	1.147-1.175	50
358	4-nitrophenol	1354	258	0.997-1.006	50
260	2-methyl-4,6-dinitrophenol-d2	1433	164	1.216-1.249	20
360	2-methyl-4,6-dinitrophenol	1435	260	1.000-1.002	20
264	Pentachlorophenol-13C6	1559	164	1.320-1.363	50
364	Pentachlorophenol	1561	264	0.998-1.002	50

¹ Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

² This is a minimum level at which the entire GC/MS system must give recognizable mass spectra (background corrected) and acceptable calibration points.

ns = specification not available at time of release of method.

Column: 30 ± 2 m × 0.25 ± 0.02 mm i.d. 94% methyl, 4% phenyl, 1% vinyl bonded phase fused silica capillary.

Temperature program: 5 min at 30 °C; 30–250 °C or until pentachlorophenol elutes.

Gas velocity: 30 ± 5 cm/sec.

TABLE 5.—DFTPP MASS INTENSITY SPECIFICATIONS

Mass	Intensity required
51	30-80 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	30-60 percent of mass 198.
197	Less than 1 percent of mass 198.
199	5-9 percent of mass 198.
275	10-30 percent of mass 198.
441	Less than mass 443.
442	40-100 percent of mass 198.
443	17-23 percent of mass 442.

TABLE 6.—BASE/NEUTRAL EXTRACTABLE COMPOUND CHARACTERISTIC MASSES

Compound	Labeled analog	Primary m/z
Acenaphthene	d10	154/164
Acenaphthylene	d8	152/160
Anthracene	d10	178/188
Benidine	d8	184/192
Benzo(a)anthracene	d12	228/240
Benzo(b)fluoranthene	d12	252/264
Benzo(k)fluoranthene	d12	252/264
Benzo(a)pyrene	d12	252/264
Benzo(ghi)perylene	d12	276/288
Biphenyl	d10	154/164
Bis(2-chloroethyl) ether	d8	93/101
Bis(2-chloroethoxy)methane		93
Bis(2-chloroisopropyl) ether	d12	121/131
Bis(2-ethylhexyl) phthalate	d4	149/153
4-bromophenyl phenyl ether		248
Butyl benzyl phthalate		149
n-C10	d22	55/66
n-C12	d26	55/66
n-C14		55
n-C16	d34	55/66

TABLE 6.—BASE/NEUTRAL EXTRACTABLE COMPOUND CHARACTERISTIC MASSES—Continued

Compound	Labeled analog	Primary m/z
n-C18		55
n-C20	d42	55/66
n-C22		55
n-C24	d50	55/66
n-C26		55
n-C28		55
n-C30	d62	55/66
Carbazole	d8	167/175
2-chloronaphthalene	d7	162/169
4-chlorophenyl phenyl ether	d5	204/209
Chrysene	d12	228/240
p-cymene	d14	114/130
Dibenzo(a,h)anthracene		278
Dibenzofuran	d8	168/176
Dibenzothiophene	d8	184/192
Di-n-butyl phthalate	d4	149/153
1,2-dichlorobenzene	d4	146/152
1,3-dichlorobenzene	d4	146/152
1,4-dichlorobenzene	d4	146/152
3,3'-dichlorobenzidine	d6	252/258
Diethyl phthalate	d4	149/153
2,4-dimethylphenol	d3	122/125
Dimethyl phthalate	d4	163/167
2,4-dinitrotoluene	d3	164/168
2,6-dinitrotoluene	d3	165/167
Di-n-octyl phthalate	d4	149/153
Diphenylamine	d10	169/179
Diphenyl ether	d10	170/180
1,2-diphenylhydrazine*	d10	77/82
Fluoranthene	d10	202/212
Fluorene	d10	166/176
Hexachlorobenzene	13C6	284/292
Hexachlorobutadiene	13C4	225/231
Hexachloroethane	13C	201/204
Hexachlorocyclopentadiene	13C4	237/241
Ideno(1,2,3-cd)pyrene		276
Isophorone	d8	82/88

TABLE 6.—BASE/NEUTRAL EXTRACTABLE COMPOUND CHARACTERISTIC MASSES—Continued

Compound	Labeled analog	Primary m/z
Naphthalene	d8	128/136
N-naphthylamine	d7	143/150
Nitrobenzene	d5	123/128
N-nitrosodimethylamine		74
N-nitrosodi-n-propylamine		70
N-nitrosodiphenylamine**	d6	169/175
Phenanthrene	d10	178/188
Phenol	d5	94/71
a-picoline	d7	93/100
Pyrene	d10	202/212
Styrene	d5	104/109
a-terpineol	d3	59/62
1,2,3-trichlorobenzene	d3	180/183
1,2,4-trichlorobenzene	d3	180/183

*Detected as azobenzene.

**Detected as diphenylamine.

TABLE 7.—ACID EXTRACTABLE COMPOUND CHARACTERISTIC MASSES

Compound	Labeled analog	Primary m/z
4-chloro-3-methylphenol	d2	107/109
2-chlorophenol	d4	129/132
2,4-dichlorophenol	d3	162/167
2,4-dinitrophenol	d3	184/187
2-methyl-4,6-dinitrophenol	d2	198/200
2-nitrophenol	d4	139/143
4-nitrophenol	d4	139/143
Pentachlorophenol	13C6	266/272
2,3,6-trichlorophenol	d2	196/200
2,4,5-trichlorophenol	d2	196/200
2,4,6-trichlorophenol	d2	196/200

TABLE 8.—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS

EGD No. 1	Compound	Acceptance criteria			
		Initial precision and accuracy section 8.2.3 (µg/L)		Labeled compound recovery sec. 8.3 and 14.2 P (percent)	On-going accuracy sec. 11.6 R (µg/L)
		s	X		
301	Acenaphthene	21	79-134		72-144
201	Acenaphthene-d10	38	38-147	20-270	30-180
377	Acenaphthylene	38	69-188		61-207
277	Acenaphthylene-d8	31	38-146	23-239	33-168
378	Anthracene	41	58-174		50-199
278	Anthracene-d10	49	31-194	14-419	23-242
305	Benidine	119	16-518		11-672
205	Benidine-d8	269	ns-ns	ns-ns	ns-ns
372	Benzo(a)anthracene	20	65-168		62-176
272	Benzo(a)anthracene-d12	41	25-298	12-605	22-329
374	Benzo(b)fluoranthene	183	32-545		20-ns
274	Benzo(b)fluoranthene-d12	168	11-577	ns-ns	ns-ns
375	Benzo(k)fluoranthene	26	59-143		53-155
275	Benzo(k)fluoranthene-d12	114	15-514	ns-ns	ns-685
373	Benzo(a)pyrene	26	62-195		59-206
273	Benzo(a)pyrene-d12	24	35-181	21-290	32-194
379	Benzo(ghi)perylene	21	72-160		58-168
279	Benzo(ghi)perylene-d12	45	29-268	14-529	25-303
712	Biphenyl (Appendix C)	41	75-148		62-176
612	Biphenyl-d12	43	28-165	ns-ns	17-267
318	Bis(2-chloroethyl) ether	34	55-196		61-164
218	Bis(2-chloroethyl) ether-d8	33	29-196	15-372	50-213
043	Bis(2-chloroethoxy)methane*	27	43-153		25-222
342	Bis(2-chloroisopropyl) ether	17	81-138		39-166
242	Bis(2-chloroisopropyl) ether-d12	27	35-149	20-260	77-145
366	Bis(2-ethylhexyl) phthalate	31	69-220		30-169
266	Bis(2-ethylhexyl) phthalate-d4	29	32-205	18-364	64-232
041	4-bromophenyl phenyl ether*	44	44-140		28-224
067	Butyl benzyl phthalate*	31	19-233		35-172
717	n-C10 (Appendix C)	51	24-195		35-170
617	n-C10-d22	70	ns-298	ns-ns	19-237
706	n-C12 (Appendix C)	74	35-369		ns-504
606	n-C12-d26	53	ns-331	ns-ns	29-424
518	n-C14 (Appendix C)	109	ns-985		ns-408
719	n-C16 (Appendix C)	33	80-162		ns-ns
619	n-C16-d34	46	37-162	18-308	71-181
520	n-C18 (Appendix C)	39	42-131		28-202
721	n-C20 (Appendix C)	59	53-263		35-167
621	n-C20-d42	34	34-172	19-306	46-301
522	n-C22 (Appendix C)	31	45-152		29-198
723	n-C24 (Appendix C)	11	80-139		39-195
623	n-C24-d50	28	27-211	15-376	78-142
524	n-C26 (Appendix C)	35	35-193		50-199
525	n-C28 (Appendix C)	35	35-193		25-229
726	n-C30 (Appendix C)	32	61-200		26-392
626	n-C30-d62	41	27-242	13-479	31-212
528	Carbazole (4c)*	38	36-165		66-152
320	2-chloronaphthalene	100	46-357		56-215
220	2-chloronaphthalene-d7	41	30-168	15-324	24-274
322	4-chloro-3-methylphenol	37	76-131		31-188
222	4-chloro-3-methylphenol-d2	111	30-174	ns-613	35-442
324	2-chlorophenol	13	79-135		62-159
224	2-chlorophenol-d4	24	38-162	23-255	14-314
340	4-chlorophenyl phenyl ether	42	75-166		76-138
240	4-chlorophenyl phenyl ether-d5	52	40-161	19-325	33-176
376	Chrysene	51	59-188		71-142
276	Chrysene-d12	69	33-219	13-512	63-194
713	p-cymene (Appendix C)	19	76-140		29-212
613	p-cymene-d14	67	ns-359	ns-ns	70-142
082	Dibenz(a,h)anthracene*	55	23-299		23-290
705	Dibenzofuran (Appendix C)	20	85-136		72-147
605	Dibenzofuran-d8	31	47-136	28-220	66-152
704	Dibenzothiophene (Synfuel)	31	79-150		13-761
604	Dibenzothiophene-d8	31	48-130	29-215	73-136
368	Di-n-butyl phthalate	15	76-165		66-150
268	Di-n-butyl phthalate-d4	23	23-195	13-346	39-160
325	1,2-dichlorobenzene	17	73-148		72-140
225	1,2-dichlorobenzene-d4	35	14-212	ns-494	69-145
326	1,3-dichlorobenzene	43	63-201		71-142
226	1,3-dichlorobenzene-d4	48	13-203	ns-550	74-169
327	1,4-dichlorobenzene	42	61-194		52-192
227	1,4-dichlorobenzene-d4	48	15-193	ns-474	74-135
328	3,3'-dichlorobenzidine	26	68-174		61-164
228	3,3'-dichlorobenzidine-d6	80	ns-562	ns-ns	85-154
331	2,4-dichlorophenol	12	85-131		55-225
231	2,4-dichlorophenol-d3	28	38-164	24-260	ns-260
370	Diethyl phthalate	44	75-196		62-161
270	Diethyl phthalate-d4	78	ns-260	ns-ns	65-153
334	2,4-dimethylphenol	13	62-153		65-153
234	2,4-dimethylphenol-d3	22	15-228	ns-449	77-130
371	Dimethyl phthalate	36	74-188		64-185
271	Dimethyl phthalate-d4	108	ns-640	ns-ns	ns-ns
359	2,4-dinitrophenol	18	72-134		50-201
259	2,4-dinitrophenol-d3	66	22-308	ns-ns	73-137
335	2,4-dinitrotoluene	18	75-158		ns-ns
235	2,4-dinitrotoluene-d3	37	22-245	10-514	68-141
336	2,6-dinitrotoluene	30	80-141		39-256
236	2,6-dinitrotoluene-d3	59	44-184	17-442	79-127
					72-164
					19-275
					55-183
					70-159
					31-250

TABLE 8.—ACCEPTANCE CRITERIA FOR PERFORMANCE TESTS—Continued

EGD No. ¹	Compound	Acceptance criteria				
		Initial precision and accuracy section 8.2.3 (µg/L)		Labeled compound recovery sec. 8.3 and 14.2 P (percent)	Calibration verification sec. 12.5 (µg/mL)	On-going accuracy sec. 11.6 R (µg/L)
		s	X			
369	Di-n-octyl phthalate.....	16	77-181		71-140	74-166
269	Di-n-octyl phthalate-d4.....	46	12-383	ns-ns	21-467	10-433
707	Diphenylamine (Appendix C).....	45	58-205		57-176	51-231
607	Diphenylamine-d10.....	42	27-206	11-488	59-169	21-249
708	Diphenyl ether (Appendix C).....	19	82-136		83-120	77-144
608	Diphenyl ether-d10.....	37	36-155	19-281	77-129	29-186
337	1,2-diphenylhydrazine.....	73	49-308		75-134	40-360
237	1,2-diphenylhydrazine-d10.....	35	31-173	17-316	58-174	26-200
339	Fluoranthene.....	33	71-177		67-149	64-194
239	Fluoranthene-d10.....	35	36-181	20-278	47-215	30-187
380	Fluorene.....	29	81-132		74-135	70-151
280	Fluorene-d10.....	43	51-131	27-238	61-164	38-172
309	Hexachlorobenzene.....	16	90-124		78-128	85-132
209	Hexachlorobenzene-13C6.....	81	36-228	13-595	38-265	23-321
352	hexachlorobutadiene.....	56	51-251		74-135	43-287
252	hexachlorobutadiene-13C4.....	63	ns-316	ns-ns	68-148	ns-413
312	hexachloroethane.....	227	21-ns		71-141	13-ns
212	hexachloroethane-13C1.....	77	ns-400	ns-ns	47-212	ns-563
353	hexachlorocyclopentadiene.....	15	69-144		77-129	67-148
253	hexachlorocyclopentadiene-13C4.....	60	ns-ns	ns-ns	47-211	ns-ns
083	ideno(1,2,3-cd)pyrene*	55	23-299		13-761	19-340
354	isophorone.....	25	76-156		70-142	70-168
254	isophorone-d8.....	23	49-133	33-193	52-194	44-147
360	2-methyl-4,6-dinitrophenol.....	19	77-133		69-145	72-142
260	2-methyl-4,6-dinitrophenol-d2.....	64	36-247	16-527	56-177	28-307
355	naphthalene.....	20	80-139		73-137	75-149
255	naphthalene-d8.....	39	28-157	14-305	71-141	22-192
702	B-naphthylamine (Appendix C).....	49	10-ns		39-256	ns-ns
602	B-naphthylamine-d7.....	33	ns-ns	ns-ns	44-230	ns-ns
356	nitrobenzene.....	25	69-161		85-115	65-169
256	nitrobenzene-d5.....	28	18-265	ns-ns	46-219	15-314
357	2-nitrophenol.....	15	78-140		77-129	75-145
257	2-nitrophenol-d4.....	23	41-145	27-217	61-163	37-158
358	4-nitrophenol.....	42	62-146		55-183	51-175
258	4-nitrophenol-d4.....	188	14-398	ns-ns	35-287	ns-ns
061	N-nitrosodimethylamine*	198	21-472		40-249	12-807
063	N-nitrosodi-n-propylamine*	198	21-472		40-249	12-807
362	N-nitrosodiphenylamine.....	45	65-142		68-148	53-173
262	N-nitrosodiphenylamine-d6.....	37	54-126	26-256	59-170	40-166
364	pentachlorophenol.....	21	76-140		77-130	71-150
264	pentachlorophenol-13C6.....	49	37-212	18-412	42-237	29-254
381	phenanthrene.....	13	93-119		75-133	87-126
281	phenanthrene-d10.....	40	45-130	24-241	67-149	34-168
365	phenol.....	36	77-127		65-155	62-154
265	phenol-d5.....	161	21-210	ns-ns	48-208	ns-ns
703	a-picoline (Synfuel).....	38	59-149		60-165	50-174
603	a-picoline-d7.....	138	11-380	ns-ns	31-324	ns-608
384	pyrene.....	19	76-152		76-132	72-159
284	pyrene-d10.....	29	32-176	18-303	48-210	28-196
710	styrene (Appendix C).....	42	53-221		65-153	48-244
610	styrene-d5.....	49	ns-281	ns-ns	44-228	ns-348
709	a-terpineol (Appendix C).....	44	42-234		54-186	38-258
609	a-terpineol-d3.....	48	22-292	ns-672	20-502	18-339
529	1,2,3-trichlorobenzene (4c)*.....	69	15-229		60-167	11-297
308	1,2,4-trichlorobenzene.....	19	82-136		78-128	77-144
208	1,2,4-trichlorobenzene-d3.....	57	15-212	ns-592	61-163	10-282
530	2,3,6-trichlorophenol (4c)*.....	30	58-137		56-180	51-153
531	2,4,5-trichlorophenol (4c)*.....	30	58-137		56-180	51-153
321	2,4,6-trichlorophenol.....	57	59-205		81-123	48-244
221	2,4,6-trichlorophenol-d2.....	47	43-183	21-363	69-144	34-226

¹ Reference numbers beginning with 0, 1 or 5 indicate a pollutant quantified by the internal standard method; reference numbers beginning with 2 or 6 indicate a labeled compound quantified by the internal standard method; reference numbers beginning with 3 or 7 indicate a pollutant quantified by isotope dilution.

* Measured by internal standard; specification derived from related compound.

ns = no specification; limit is outside the range that can be measured reliably.

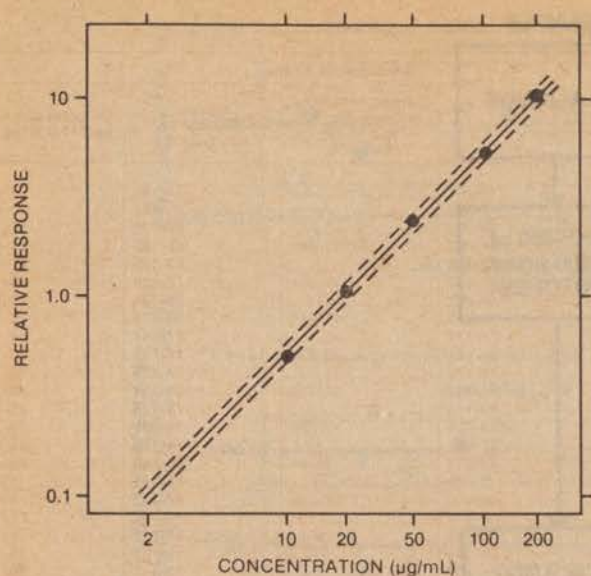


FIGURE 1 Relative Response Calibration Curve for Phenol. The Dotted Lines Enclose a ± 10 Percent Error Window.

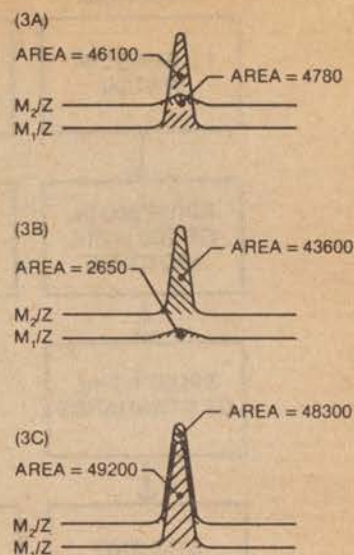


FIGURE 3 Extracted Ion Current Profiles for (3A) Unlabeled Compound, (3B) Labeled Compound, and (3C) Equal Mixture of Unlabeled and Labeled Compounds.

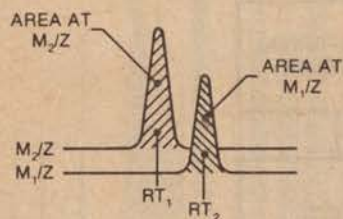


FIGURE 2 Extracted Ion Current Profiles for Chromatographically Resolved Labeled (m_2/z) and Unlabeled (m_1/z) Pairs.

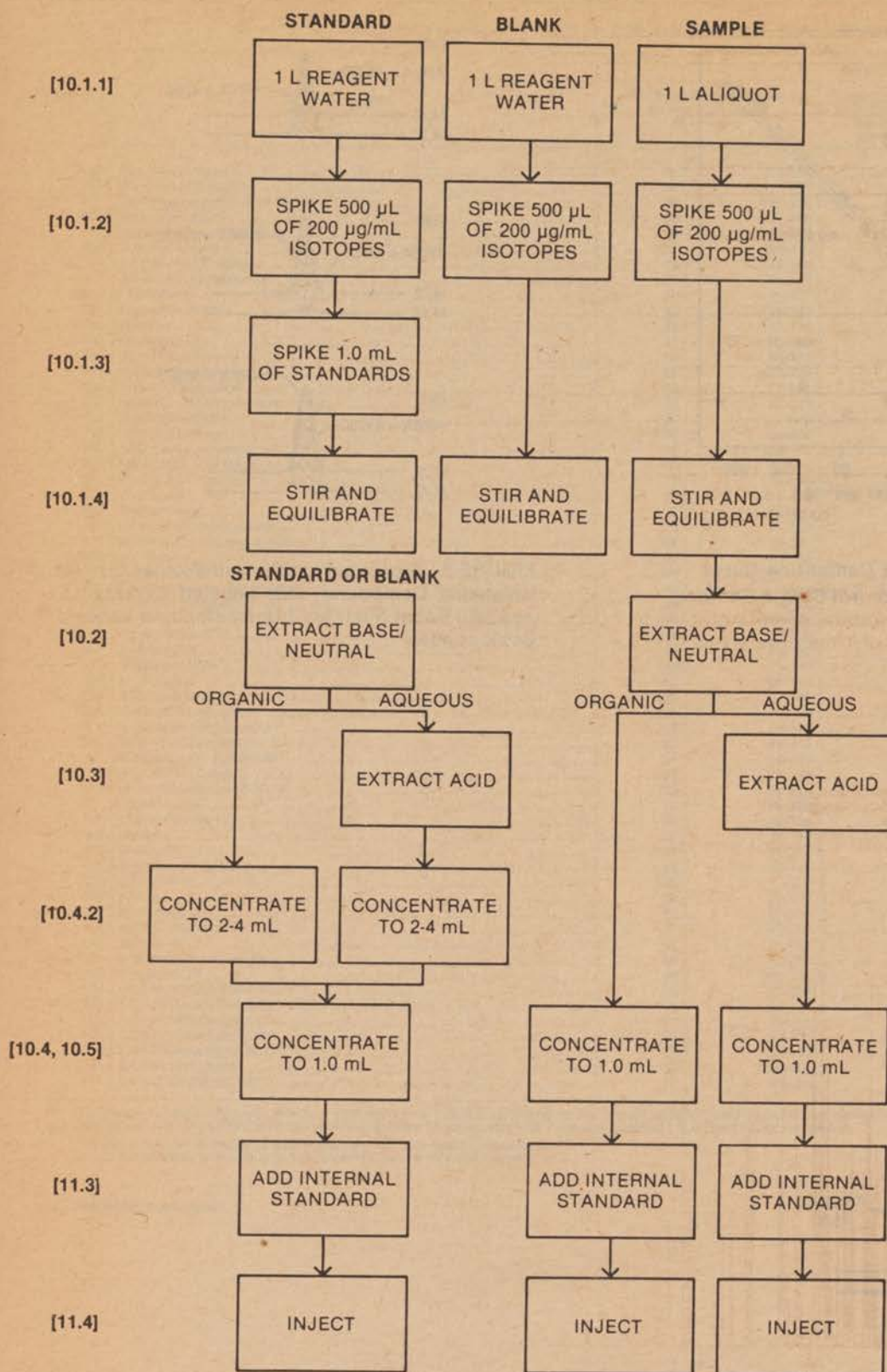


FIGURE 4 Flow Chart for Extraction/Concentration of Precision and Recovery Standard, Blank, and Sample by Method 1625. Numbers in Brackets [] Refer to Section Numbers in the Method.

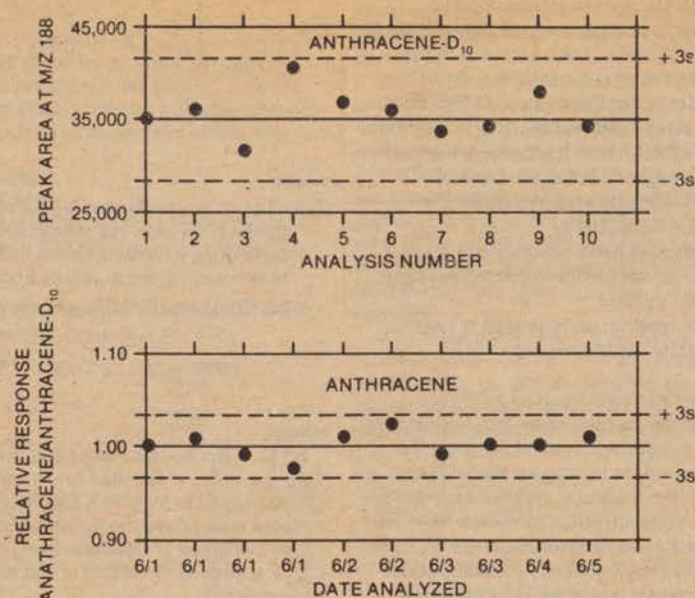


FIGURE 5 Quality Control Charts Showing Area (top graph) and Relative Response of Anthracene to Anthracene-d₁₀ (lower graph) Plotted as a Function of Time or Analysis Number.

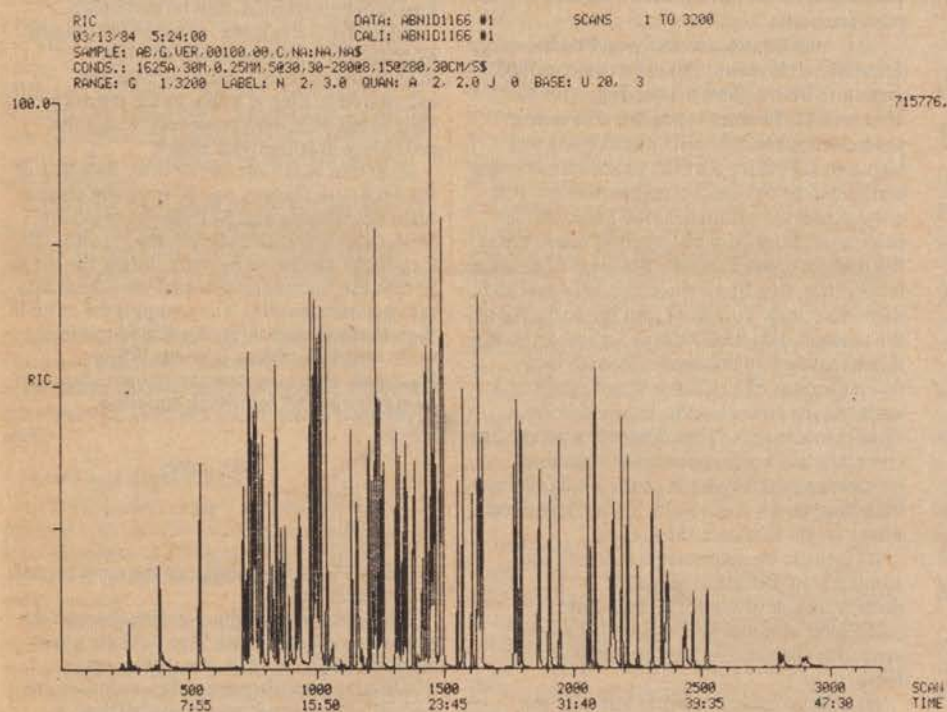


FIGURE 6 Chromatogram of Combined Acid/base/neutral Standard.

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Appendix B to Part 136—Definition and Procedure for the Determination of the Method Detection Limit—Revision 1.11

Definition

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.

(b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.

(c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

(d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated method detection limit. (Recommend between 1 and 5 times the estimated method detection limit.) Proceed to Step 4.

(b) If the MDL is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

(1) Obtain another sample with a lower level of analyte in the same matrix if possible.

(2) The sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.

4. (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.

(b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:

(1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.

(2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.

5. Calculate the variance (S^2) and standard deviation (S) of the replicate measurements, as follows:

$$S^2 = \frac{1}{n-1} \left[\sum_{i=1}^n x_i^2 - \left(\frac{\sum_{i=1}^n x_i}{n} \right)^2 \right] / n$$

$$S = (S^2)^{1/2}$$

where:

X_i , $i=1$ to n , = are the analytical results in the final method reporting units obtained from the n sample aliquots and Σ refers to the sum of the X values from $i=1$ to n .

6. (a) Compute the MDL as follows:

$$MDL = t_{(n-1, 1-\alpha = 0.99)} (S) \quad (S)$$

where:

MDL = the method detection limit
 $t_{(n-1, 1-\alpha = 0.99)}$ = the student's t value appropriate for a 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom. See Table.
 S = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution (χ^2/df).

$$LCL = 0.64 MDL$$

$$UCL = 2.20 MDL$$

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike in the matrix at the calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use S^2 from the current MDL calculation and S^2 from the previous MDL calculation to compute the F -ratio. The F -ratio is calculated by substituting the larger S^2 into the numerator S_A^2 and the others into the denominator S_B^2 . The computed F -ratio is then compared with the F -ratio found in the table which is 3.05 as follows: if $S_A^2/S_B^2 < 3.05$, then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[\frac{6S_A^2 + 6S_B^2}{12} \right]^{1/2}$$

if $S_A^2/S_B^2 > 3.05$, respike at the most recent calculated

MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the S_{pooled} as calculated in 7b to compute the final MDL according to the following equation:

MDL = 2.681 (S_{pooled})

where 2.681 is equal to $t_{(12, 1 - 0.99)}$

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

LCL = 0.72 MDL

UCL = 1.65 MDL

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' *t* VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n, 1 - 0.99)}$
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
26	25	2.485
31	30	2.457
61	60	2.390
00	00	2.326

Reporting

The analytical method used must be specifically identified by number or title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or does not exceed 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

Appendix C to Part 136—Inductively Coupled Plasma—Atomic Emission Spectrometric Method for Trace Element Analysis of Water and Wastes Method 200.7

1. Scope and Application

1.1 This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L. (See section 5.)

1.3 Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the

samples, appropriate steps must be taken to correct for potential interference effects. (See section 5.)

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary. In time, other elements may be added as more information becomes available and as required.

1.5 Because of the differences between various makes and models of satisfactory instruments, no detailed instrumental operating instructions can be provided. Instead, the analyst is referred to the instruction provided by the manufacturer of the particular instrument.

2. Summary of Method

2.1 The method describes a technique for the simultaneous or sequential multielement determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in 5.1 (and tests for their presence as described in 5.2) should also be recognized and appropriate corrections made.

3. Definitions

3.1 *Dissolved*—Those elements which will pass through a 0.45 μm membrane filter.

3.2 *Suspended*—Those elements which are retained by a 0.45 μm membrane filter.

3.3 *Total*—The concentration determined on an unfiltered sample following vigorous digestion (Section 9.3), or the sum of the dissolved plus suspended concentrations. (Section 9.1 plus 9.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 9.4).

3.5 *Instrumental detection limit*—The concentration equivalent to a signal, due to the analyte, which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

3.6 *Sensitivity*—The slope of the analytical curve, i.e. functional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst to monitor and verify instrument performance on a daily basis. (See 7.6.1)

3.8 *Interference check sample*—A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors. (See 7.6.2.)

3.9 *Quality control sample*—A solution obtained from an outside source having known, concentration values to be used to verify the calibration standards. (See 7.6.3)

3.10 *Calibration standards*—A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve). (See 7.4)

3.11 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.12 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 7.5.2)

3.13 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl . (See 7.5.1)

3.14 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 10.6.1.)

4. Safety

4.1 The toxicity of carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified (14.7, 14.8 and 14.9) for the information of the analyst.

5. Interferences

5.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

5.1.1 *Spectral interferences* can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from

the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array. Listed in Table 2 are some interference effects for the recommended wavelengths given in Table 1. The data in Table 2 are intended for use only as a rudimentary guide for the indication of potential spectral interferences. For this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed. The Interference information, which was collected at the Ames Laboratory,¹ is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interferent element. The suggested use of this information is as follows: Assume that arsenic (at 193.696 nm) is to be determined in a sample containing approximately 10 mg/L of aluminum. According to Table 2, 100 mg/L of aluminum would yield a false signal for arsenic equivalent to approximately 1.3 mg/L. Therefore, 10 mg/L of aluminum would result in a false signal for arsenic equivalent to approximately 0.13 mg/L. The reader is cautioned that other analytical systems may exhibit somewhat different levels of interference than those shown in Table 2, and that the interference effects must be evaluated for each individual system.

Only those interferents listed were investigated and the blank spaces in Table 2 indicate that measurable interferences were not observed for the interferent concentrations listed in Table 3. Generally, interferences were discernible if they produced peaks or background shifts corresponding to 2-5% of the peaks generated by the analyte concentrations also listed in Table 3.

At present, information on the listed silver and potassium wavelengths are not available but it has been reported that second order energy from the magnesium 383.231 nm wavelength interferes with the listed potassium line at 766.491 nm.

5.1.2 *Physical interferences* are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques. Another problem which can

occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

5.1.3 *Chemical Interferences* are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.2 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 5.2.1 through 5.2.4, will ensure the analyst that neither positive nor negative interference effects are operative on any of the analyte elements thereby distorting the accuracy of the reported values.

5.2.1 *Serial dilution*—If the analyte concentration is sufficiently high (minimally a factor of 10 above the instrumental detection limit after dilution), an analysis of a dilution should agree within 5 percent of the original determination (or within some acceptable control limit (14.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

5.2.2 *Spike addition*—The recovery of a spike addition added at a minimum level of 10X the instrumental detection limit (maximum 100X) to the original determination should be recovered to within 90 to 110 percent or within the established control limit for that matrix. If not, a matrix effect should be suspected. The use of a standard addition analysis procedure can usually compensate for this effect.

Caution: The standard addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended (See 5.2.3).

5.2.3 *Comparison with alternate method of analysis*—When investigating a new sample matrix, comparison tests may be performed with other analytical techniques such as atomic absorption spectrometry, or other approved methodology.

5.2.4 *Wavelength scanning of analyte line region*—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

6. Apparatus

6.1 Inductively Coupled Plasma-Atomic Emission Spectrometer.

6.1.1 Computer controlled atomic emission spectrometer with background correction.

6.1.2 Radiofrequency generator.

6.1.3 Argon gas supply, welding grade or better.

6.2 *Operating conditions*—Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain quality control data confirming instrument performance and analytical results.

7. Reagents and Standards

7.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

7.1.1 *Acetic acid*, conc. (sp gr 1.06).

7.1.2 *Hydrochloric acid*, conc. (sp gr 1.19).

7.1.3 *Hydrochloric acid*, (1+1): Add 500 mL conc. HCl (sp gr 1.19) to 400 mL deionized, distilled water and dilute to 1 liter.

7.1.4 *Nitric acid*, conc. (sp gr 1.41).

7.1.5 *Nitric acid*, (1+1): Add 500 mL conc. HNO₃ (sp gr 1.41) to 400 mL deionized, distilled water and dilute to 1 liter.

7.2 *Deionized, distilled water*: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized, distilled water for the preparation of all reagents, calibration standards and as dilution water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification D 1193 (14.8).

7.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals. All salts must be dried for 1 h at 105 °C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.)

Typical stock solution preparation procedures follow:

7.3.1 *Aluminum solution, stock*, 1 mL = μ g Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask add an additional 10 mL of (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.2 *Antimony solution stock*, 1 mL = 100 μ g Sb: Dissolve 0.2669 g K(SbO)C₄H₄O₆ in deionized distilled water, add 10 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.3 *Arsenic solution, stock*, 1 mL = 100 μ g As: Dissolve 0.1320 g of As₂O₃ in 100 mL of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

¹Ames Laboratory, USDOE, Iowa State University, Ames Iowa 50011.

7.3.4 *Barium solution, stock*, 1 mL=100 µg Ba: Dissolve 0.1516 g BaCl₂ (dried at 250 °C for 2 hrs) in 10 mL deionized, distilled water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.5 *Beryllium solution, stock*, 1 mL=100 µg Be: Do not dry. Dissolve 1.966 g BeSO₄·4H₂O in deionized, distilled water, add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.6 *Boron solution, stock*, 1 mL=100 µg B: Do not dry. Dissolve 0.5716 g anhydrous H₃BO₃ in deionized, distilled water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered and store in a desiccator to prevent the entrance of atmospheric moisture.

7.3.7 *Cadmium solution, stock*, 1 mL=100 µg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.8 *Calcium solution, stock*, 1 mL=100 µg Ca: Suspend 0.2498 g CaCO₃ dried at 180 °C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.9 *Chromium solution, stock*, 1 mL=100 µg Cr: Dissolve 0.1923 g of CrO₃ in deionized, distilled water. When solution is complete, acidify with 10 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.10 *Cobalt solution, stock*, 1 mL=100 µg Co: Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO₃. Add 10.0 mL (1+1) HCl and dilute to 1,000 mL with deionized, distilled water.

7.3.11 *Copper solution, stock*, 1 mL=100 µg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.12 *Iron solution, stock*, 1 mL=100 µg Fe: Dissolve 0.1430 g Fe₂O₃ in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO₃. Cool, add an additional 5 mL of conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.13 *Lead solution, stock*, 1 mL=100 µg Pb: Dissolve 0.1599 g Pb(NO₃)₂ in a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.14 *Magnesium solution, stock*, 1 mL=100 µg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.15 *Manganese solution, stock*, 1 mL=100 µg Mn: Dissolve 0.1000 g of manganese metal in the acid mixture 10 mL conc. HCl and 1 mL conc. HNO₃, and dilute to 1,000 mL with deionized, distilled water.

7.3.16 *Molybdenum solution, stock*, 1 mL=100 µg Mo: Dissolve 0.2043 g (NH₄)₂MoO₄ in deionized, distilled water and dilute to 1,000 mL.

7.3.17 *Nickel solution, stock*, 1 mL=100 µg Ni: Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO₃, cool and dilute to 1,000 mL with deionized, distilled water.

7.3.18 *Potassium solution, stock*, 1 mL=100 µg K: Dissolve 0.1907 g KCl, dried at 110 °C, in deionized, distilled water and dilute to 1,000 mL.

7.3.19 *Selenium solution, stock*, 1 mL=100 µg Se: Do not dry. Dissolve 0.1727 g H₂SeO₃ (actual assay 94.6%) in deionized, distilled water and dilute to 1,000 mL.

7.3.20 *Silica solution, stock*, 1 mL=100 µg SiO₂: Do not dry. Dissolve 0.4730 g Na₂SiO₃·9H₂O in deionized, distilled water. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.21 *Silver solution, stock*, 1 mL=100 µg Ag: Dissolve 0.1575 g AgNO₃ in 100 mL of deionized, distilled water and 10 mL conc. HNO₃. Dilute to 1,000 mL with deionized, distilled water.

7.3.22 *Sodium solution, stock*, 1 mL=100 µg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.23 *Thallium solution, stock*, 1 mL=100 µg Tl: Dissolve 0.1303 g TlNO₃ in deionized, distilled water. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.24 *Vanadium solution, stock*, 1 mL=100 µg V: Dissolve 0.2297 g NH₄VO₃ in a minimum amount of conc. HNO₃. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL with deionized, distilled water.

7.3.25 *Zinc solution, stock*, 1 mL=100 µg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO₃. Add 10.0 mL conc. HNO₃ and dilute to 1,000 mL deionized, distilled water.

7.4 *Mixed calibration standard solutions*—Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 7.4.1 thru 7.4.5) Add 2 mL of (1+1) HNO₃ and 10 mL of (1+1) HCl and dilute to 100 mL with deionized, distilled water. (See Notes 1 and 6.) Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored weekly for stability (See 7.6.3). Although not specifically required, some typical calibration standard combinations follow when using those specific wavelengths listed in Table 1.

7.4.1 *Mixed standard solution I*—Manganese, beryllium, cadmium, lead, and zinc.

7.4.2 *Mixed standard solution II*—Barium, copper, iron, vanadium, and cobalt.

7.4.3 *Mixed standard solution III*—Molybdenum, silica, arsenic, and selenium.

7.4.4 *Mixed standard solution IV*—Calcium, sodium, potassium, aluminum, chromium and nickel.

7.4.5 *Mixed standard solution V*—Antimony, boron, magnesium, silver, and thallium.

Note 1.—If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of deionized distilled water and warm the flask until the solution clears. Cool and dilute to 100 mL with deionized, distilled water. For this acid combination the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.5 Two types of blanks are required for the analysis. The calibration blank (3.13) is used in establishing the analytical curve while the reagent blank (3.12) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

7.5.1 *The calibration blank* is prepared by diluting 2 mL of (1+1) HNO₃ and 10 mL of (1+1) HCl to 100 mL with deionized, distilled water. (See Note 6.) Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.5.2 *The reagent blank* must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.6 In addition to the calibration standards, an instrument check standard (3.7), an interference check sample (3.8) and a quality control sample (3.9) are also required for the analyses.

7.6.1 *The instrument check standard* is prepared by the analyst by combining compatible elements at a concentration equivalent to the midpoint of their respective calibration curves. (See 12.1.1.)

7.6.2 *The interference check sample* is prepared by the analyst in the following manner. Select a representative sample which contains minimal concentrations of the analytes of interest but known concentration of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at the approximate concentration of either 100 µg/L or 5 times the estimated detection limits given in Table 1. (For effluent samples of expected high concentrations, spike at an appropriate level.) If the type of samples analyzed are varied, a synthetically prepared sample may be used if the above criteria and intent are met. A limited supply of a synthetic interference check sample will be available from the Quality Assurance Branch of EMSL-Cincinnati. (See 12.1.2.)

7.6.3 *The quality control sample* should be prepared in the same acid matrix as the calibration standards at a concentration near 1 mg/L and in accordance with the instructions provided by the supplier. The Quality Assurance Branch of EMSL-Cincinnati will either supply a quality control sample or information where one of equal quality can be procured. (See 12.1.3.)

8. Sample Handling and Preservation

8.1 For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. Laboratory glassware including the sample bottle (whether polyethylene, polypropylene or FEP-fluorocarbon) should be thoroughly washed with detergent and tap water; rinsed with (1+1) nitric acid, tap water, (1+1) hydrochloric acid, tap and finally deionized, distilled water in that order (See Notes 2 and 3).

Note 2.—Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product, NOCHROMIX, available from Godax Laboratories, 6 Varick St., New York, NY 10013, may be used in place of chromic acid. Chromic acid should not be used with plastic bottles.

Note 3.—If it can be documented through an active analytical quality control program using spiked samples and reagent blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

8.2 Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter.

8.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45- μ m membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Use the first 50–100 mL to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to a pH of 2 or less. Normally, 3 mL of (1+1) acid per liter should be sufficient to preserve the sample.

8.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45- μ m membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

8.2.3 For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO_3 to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

9. Sample Preparation

9.1 For the determinations of dissolved elements, the filtered, preserved sample may often be analyzed as received. The acid matrix and concentration of the samples and calibration standards must be the same. (See Note 6.) If a precipitate formed upon acidification of the sample or during transit or storage, it must be redissolved before the analysis by adding additional acid and/or by heat as described in 9.3.

9.2 For the determination of suspended elements, transfer the membrane filter containing the insoluble material to a 150-mL Griffin beaker and add 4 mL conc. HNO_3 . Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 mL of conc. HNO_3 . Cover and continue heating until the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (2 mL), cool, and 10 mL HCl (1+1) and 15 mL deionized, distilled water per 100 mL dilution and warm the beaker gently for 15 min. to dissolve any precipitated or residue material. Allow to cool, wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined (See Note 6). The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

Note 4.—In place of filtering, the sample after diluting and mixing may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

9.3 For the determination of total elements, choose a measured volume of the well mixed acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 3 mL of conc. HNO_3 . Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil and that no area of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 5 mL portion of conc. HNO_3 . Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gently reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing.) Again, evaporate to near dryness and cool the beaker. Add 10 mL of 1+1 HCl and 15 mL of deionized, distilled water per 100 mL of final solution and warm the beaker gently for 15 min. to dissolve any precipitate or residue resulting from evaporation. Allow to cool, wash down the beaker walls and watch glass with deionized distilled water and filter the sample to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the sample to a predetermined volume based on the expected concentrations of elements present.

The sample is now ready for analysis (See Note 6). Concentrations so determined shall be reported as "total."

Note 5.—If low determinations of boron are critical, quartz glassware should be used.

Note 6.—If the sample analysis solution has a different acid concentration from that given in 9.4, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

9.4 For the determination of total recoverable elements, choose a measured volume of a well mixed, acid preserved sample appropriate for the expected level of elements and transfer to a Griffin beaker. (See Note 5.) Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample and heat on a steam bath or hot plate until the volume has been reduced to near 25 mL making certain the sample does not boil. After this treatment, cool the sample and filter to remove insoluble material that could clog the nebulizer. (See Note 4.) Adjust the volume to 100 mL and mix. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

10. Procedure

10.1 Set up instrument with proper operating parameters established in Section 6.2. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 min. of operation prior to calibration.

10.2 Initiate appropriate operating configuration of computer.

10.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 7.4. Flush the system with the calibration blank (7.5.1) between each standard. (See Note 7.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

Note 7.—For boron concentrations greater than 500 $\mu\text{g/L}$ extended flush times of 1 to 2 minutes may be required.

10.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than +5 percent (or the established control limits whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

10.5 Begin the sample run flushing the system with the calibration blank solution (7.5.1) between each sample. (See Note 7.) Analyze the instrument check standard (7.6.1) and the calibration blank (7.5.1) each 10 samples.

10.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

10.6.1 The standard addition technique (14.2) involves preparing new standards in the sample matrix by adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal thus

producing a different slope from that of the calibration standards. It will not correct for additive interference which causes a baseline shift. The simplest version of this technique is the single-addition method. The procedure is as follows. Two identical aliquots of the sample solution, each of volume V_x , are taken. To the first (labeled A) is added a small volume V_s of a standard analyte solution of concentration c_s . To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration c_x is calculated:

$$c_x = \frac{S_B V_s c_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_x and c_s should be chosen so that S_A is roughly twice S_B on the average. It is best if V_s is made much less than V_x , and thus c_s is much greater than c_x , to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results from this technique to be valid, the following limitations must be taken into consideration:

1. The analytical curve must be linear.
2. The chemical form of the analyte added must respond the same as the analyte in the sample.
3. The interference effect must be constant over the working range of concern.
4. The signal must be corrected for any additive interference.

11. Calculation

11.1 Reagent blanks (7.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

11.2 If dilutions were performed, the appropriate factor must be applied to sample values.

11.3 Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

12. Quality Control (Instrumental)

12.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

12.1.1 Analyze and appropriate instrument check standard (7.6.1) containing the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within $\pm 5\%$ of the expected values or within the established control limits, whichever is lower, the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Analyze the calibration blank (7.5.1) at a frequency of 10%. The result should be within the established control limits of 2 standard deviations of the mean value. If not, repeat the analysis two more times and average the three results. If the average is not within the control limit, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.2 To verify interelement and background correction factors analyze the interference check sample (7.6.2) at the beginning, end, and at periodic intervals throughout the sample run. Results should fall within the established control limits of 1.5 times the standard deviation of the mean value. If not, terminate the analysis, correct the problem and recalibrate the instrument.

12.1.3 A quality control sample (7.6.3) obtained from an outside source must first be used for the initial verification of the calibration standards. A fresh dilution of this sample shall be analyzed every week thereafter to monitor their stability. If the results are not within $\pm 5\%$ of the true value listed for the control sample, prepare a new calibration standard and recalibrate the instrument. If this does not correct the problem, prepare a new stock standard and a new calibration standard and repeat the calibration.

13. Precision and Accuracy

13.1 In an EPA round robin phase 1 study, even laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table 4 lists the true value, the mean reported value and the mean % relative standard deviation.

14. References

14.1 Winge, R.K., V.J. Peterson, and V.A. Fassel, "Inductively Coupled Plasma-Atomic Emission Spectroscopy: Prominent Lines," EPA-600/4-79-017.

14.2 Winefordner, J.D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. 46, pp. 41-42.

14.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

14.4 Garbner, J.R. and Taylor, H.E., "An Inductively-Coupled Plasma Atomic Emission Spectrometric Method for Routine Water Quality Testing," *Applied Spectroscopy* 33, No. 3 (1979).

14.5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

14.6 Annual Book of ASTM Standards, Part 31.

14.7 "Carcinogens—Working With Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977.

14.8 "OSHA Safety and Health Standards, General Industry," (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

14.9 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

TABLE 1.—RECOMMENDED WAVELENGTHS¹ AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Element	Wave-length, nm	Estimated detection limit, $\mu\text{g/L}$ ²
Aluminum	308.215	45
Arsenic	193.696	53
Antimony	206.833	32
Barium	455.403	2
Beryllium	313.042	0.3
Boron	249.773	5
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Potassium	766.491	3
Selenium	196.026	75
Silica (SiO ₂)	288.158	58
Silver	328.068	7
Sodium	588.995	29
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

¹The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 5.1.1).

²The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA-600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

³Highly dependent on operating conditions and plasma position.

TABLE 1.—ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL

Analyte	Wave-length, nm	Interferent—									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Aluminum	308.214							0.21			1.4
Antimony	206.833	0.47		2.9		0.08				0.25	0.45
Arsenic	193.696	1.3		0.44							1.1
Barium	455.403										
Beryllium	313.042									0.04	0.05
Boron	249.773	0.04				0.32					
Cadmium	226.502					0.03					
Calcium	317.933			0.08		0.01	0.01	0.04	0.02	0.03	0.03
Chromium	267.716					0.003		0.04			0.04
Cobalt	228.616			0.03		0.005			0.03	0.15	
Copper	324.754					0.003				0.05	0.02

TABLE 1.—ANALYTE CONCENTRATION EQUIVALENTS (MG/L) ARISING FROM INTERFERENTS AT THE 100 MG/L LEVEL—Continued

Analyte	Wave-length, nm	Interferent—									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Ti	V
Iron	259.940							0.12			
Lead	220.353	0.17									
Magnesium	279.079		0.02	0.11		0.13		0.25		0.07	0.12
Manganese	257.610	0.005		0.01		0.002					
Molybdenum	202.030	0.05				0.03					
Nickel	231.604										
Selenium	196.026	0.23				0.09					
Silicon	288.158			0.07							0.01
Sodium	588.995									0.08	
Thallium	190.864	0.30									
Vanadium	292.402			0.05		0.005				0.02	
Zinc	213.856				0.14				0.29		

TABLE 3. INTERFERENT AND ANALYTE ELEMENTAL CONCENTRATIONS USED FOR INTERFERENCE MEASUREMENTS IN TABLE 2

Analytes		(mg/L)	Interferents		(mg/L)
Al	10		Al	1,000	
As	10		Ca	1,000	
B	10		Cr	200	
Ba	1		Cu	200	
Be	1		Fe	1,000	
Ca	1		Mg	1,000	
Cd	10		Mn	200	
Co	1		Ni	200	
Cr	1		Ti	200	
Cu	1		V	200	
Fe	1				
Mg	1				
Mn	1				
Mo	10				
Na	10				
Ni	10				
Pb	10				
Sb	10				
Se	10				
Si	1				
Ti	10				
V	1				
Zn	10				

TABLE 4.—ICP PRECISION AND ACCURACY DATA

Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True value $\mu\text{g/L}$	Mean reported value $\mu\text{g/L}$	Mean percent RSD	True value $\mu\text{g/L}$	Mean reported value $\mu\text{g/L}$	Mean percent RSD	True value $\mu\text{g/L}$	Mean reported value $\mu\text{g/L}$	Mean percent RSD
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	500	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	18	19	45	80	82	9.4
Se	40	32	21.9	6	8.5	42	10	8.5	8.3

Not all elements were analyzed by all laboratories.

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ENVIRONMENTAL PROTECTION AGENCY**40 CFR Part 136**

[FRL-2636-6]

Guidelines Establishing Test Procedures for the Analysis of Pollutants**AGENCY:** Environmental Protection Agency (EPA).**ACTION:** Proposed regulation.

SUMMARY: Elsewhere in this issue of the *Federal Register*, EPA has promulgated new test procedures under Clean Water Act (CWA) Section 304(h) for the analysis of many priority toxic organic and other pollutants, which are based upon gas chromatographic instrumental systems. This proposal would withdraw approval for outdated test procedures which had been approved for sixteen compounds, including chlorinated organic compounds, benzidine, and for fourteen pesticide compounds. EPA is also proposing to approve two methods (Methods 1624 and 1625) for new compounds. These methods were promulgated for other compounds elsewhere in today's *Federal Register*.

DATE: Comments on this proposal must be submitted on or before January 10, 1985.

ADDRESS: Send comments to Dr. Robert B. Medz, "Proposed 304(h) Guidelines," Water and Waste Management Monitoring Research Division, Office of Research and Development (RD-680), 401 M Street, SW., Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT: Dr. Robert B. Medz at the address listed above, or call (202) 382-5788. The record for the rulemaking is available for review at Washington, D.C.

SUPPLEMENTARY INFORMATION:**I. Authority and Background**

This regulation is proposed under the authority of sections 301, 304(h) and 501(a) of the Clean Water Act of 1977 (CWA).

It would amend 40 CFR Part 136 in two ways. First, it would withdraw approval of outmoded methods for the analysis of 30 chemical compounds. Second, it would expand the scope of two recently approved methods to include thirty-two additional compounds for which no approved methods now exist.

Elsewhere in today's *Federal Register*, EPA has approved new test procedures for the analysis of 111 priority, toxic organic pollutants. The analytical test procedures are based on 12 gas

chromatograph (GC) methods and 5 gas chromatograph/mass spectrometer (GC/MS) methods. These test procedures differ from those previously approved by the EPA at 40 CFR Part 136. Their most important improvement is that they include detailed quality control requirements and specify control limits indicating inadequate performance. If an analyst's performance falls outside those control limits, his analytical system is considered to be out-of-control and data generated with the system is not reportable for regulatory purposes.

EPA approved analytical methods for 3 classes of organic pollutants on December 1, 1976 (41 FR 25780). These classes included 30 compounds which were later included within the scope of the priority pollutants. The 1976 test procedures had neither detailed quality control requirements nor warning limits within their provisions. In complex industrial and municipal wastewater matrices, application of these 1976 test procedures results in data of poorly defined quality if the analyst fails to perform an adequate level of quality control. The procedures were updated in 1978 but the underlying problems with quality control were not addressed. Therefore, for the 30 organic compounds, there is an inconsistency between the test procedures approved in 1976 and the test procedures approved today. This proposal will withdraw approval for the test procedures as they apply to these 30 pollutants. In effect, the old GC procedures will be superseded by the 15 test procedures which have been approved today for the 111 priority toxic organic pollutants.

EPA has approved two GC/MS test procedures (Methods 1624 and 1625) today. These methods use stable, isotopically labeled analogs of the priority pollutants as internal standards. They have been extensively tested for their applicability to the analysis of the 32 pollutants included pursuant to paragraph 4(c) and Appendix C of the Consent Decree (NRDC v. Train, 8 ERC 2120 (D.D.C. 1976), as modified 12 ERC 1833 (D.D.C. 1979) and by the Court's Order of October 26, 1982, August 2, 1983, January 6, 1984, and July 5, 1984). The Consent Decree settled a suit between the Natural Resources Defense Council (NRDC) and EPA regarding regulation under the CWA. In paragraph 4(c), EPA agreed to study pollutants for possible regulation, including those specified in Appendix C. Today's proposal would extend the approved scope of the two methods to include the additional paragraph 4(c) and Appendix C pollutants.

II. Summary and Rationale for Proposed Amendments**A. Withdrawal of Former Method Approvals**

Thirty compounds which were approved as parameters in the 1976 amendments to 40 CFR Part 136 were also included in the 1976 Consent Decree as priority pollutants. In the 1976 regulation they were carried under the parameter designations Benzidine, Pentachlorophenol, Chlorinated organic compounds (except pesticides), and Pesticides. Approved test procedures for these parameters were available from EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio. The method for Benzidine was covered under "Method for Benzidine and Its Salts in Wastewater." The remaining parameters were covered under "Procedures for Pentachlorophenol, Chlorinated Organic Compounds, and Pesticides."

These analytical methods were updated in 1978 by the EPA publication, "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol, and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September 1978. However, the earlier methods and the 1978 update do not require a mandatory level of quality control and do not stipulate analytical control limits, outside of which an analysis would be considered to be out-of-control. Therefore, the analyst could generate data which would be unusable for regulatory purposes. The new methods being approved today for priority pollutant analysis do include these procedures. This leads to a significant inconsistency between these new methods and the updated methods which had not been anticipated at the time that the priority pollutant test procedures were proposed on December 3, 1979 (44 FR 69464).

The present proposed action will eliminate this inconsistency and ensure that these earlier methods will be superseded by the test procedures being approved today for the priority pollutants for the following specific parameters in Tables IC and ID of § 136.3: Table IC, Benzidine, Carbon Tetrachloride, Chlorobenzene, Chloroform, Methylene chloride, PCB-1016, PCB-1221, PCB-1232, PCB-1242, PCB-1248, PCB-1260, Pentachlorophenol, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, 1,2,4-Trichlorobenzene, and 1,1,2-Trichloroethane; and Table ID, Aldrin, α -BHC, γ -BHC, Chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan

I, Endosulfan II, Endrin, Heptachlor, Heptachlor epoxide, and Toxaphene.

The methods approved in 1976 and updated in 1978 may continue to be the basis for EPA enforcement action where proper quality control and quality assurance are used. Of course, EPA may also use the new methods where they are more appropriate or more economical.

B. Extension of New Methods to Appendix C Parameters

EPA is proposing to expand Table IC of § 136.3 by 32 paragraph 4(c) and Appendix C parameters (it will now include 129 parameters). The purge and trap test procedure, Method 1624, is approved for four of these purgeable compounds: Acetone, Diethyl ether, p-Dioxane, and Methyl ethyl ketone. Extraction test procedure, Method 1625, is approved for 28 compounds: Benzoic acid, Biphenyl, Carbazole, p-Cymene, n-Decane, Dibenzofuran, Dibenzothiophene, Diphenylamine, Diphenyl ether, 1,2-Diphenylhydrazine, n-Docosane, n-Dodecane, n-Eicosane, n-Hexacosane, n-Hexadecane, Hexanoic acid, β -Naphthylamine, n-Octacosane, n-Octadecane, α -Picoline, Styrene, α -Terpineol, n-Tetracosane, n-Tetradecane, n-Triacontane, 1,2,3-Trichlorobenzene, 2,3,6-Trichlorophenol, and 2,4,5-Trichlorophenol. These methods have been extensively applied to the analysis of these 32 compounds in industrial wastewaters and the methods have been validated for their applicability to analysis of these compounds by multi-laboratory testing.

C. Other Part 136 Provisions

EPA wishes to make clear that methods for the 32 new compounds that will be covered under Part 136 will be subject to all the existing definitions and provisions of Part 136. For example, EPA will be able to approve equivalent methods for these new compounds, as it can for any parameter subject to this Part.

III. Regulatory Analysis

(a) Under Executive Order 12291, EPA must judge whether a regulation is "major" and, therefore, subject to the requirement of a "Regulatory Impact Analysis." This regulation is not major for the following reasons:

(1) It proposes analytical methods and sample handling requirements that ensure a uniform measure of pollutants across all wastewater discharges within minimum acceptance criteria for 32 parameters. The purpose is to ensure that the quality of environmental monitoring data meets certain minimum

standards. It would withdraw the use of outdated methods.

(2) The impact of this regulation will be far less than \$100 million.

a. The regulation affects unit monitoring costs for other regulatory programs, e.g., effluent guidelines regulations and the implementation regulations of the National Pollutant Discharge Elimination System (NPDES), and the pretreatment program. However, it does not impose those costs. In fact, the monitoring costs for other programs are considered in those other rulemakings. This is appropriate because total (rather than unit) monitoring costs are determined by the monitoring provisions of those regulations.

b. Equivalency provisions will encourage the development of innovative analytical methods by the private sector and to encourage the competitive viability of the instrument manufacturing industry. The equivalency provision also allows individual dischargers to gain approval of analytical systems of their own design that may further reduce their total monitoring costs.

(3) The impact of compliance with these regulations will not be concentrated on any particular sectors of American industry.

This regulation was submitted to the Office of Management and Budget (OMB) for review as required by Executive Order 12291. Any comments from OMB to EPA and any EPA response to those comments will be available for public inspection at the Public Information Reference Unit, Room M2904 (EPA Library-Rear), TM-213, Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460, Phone: (202) 382-5926, Office Hours 8:00 a.m. to 4:30 p.m.

(b) Under the Regulatory Flexibility Act, 5 U.S.C. 601, *et seq.*, EPA is required to determine whether a regulation will significantly affect a substantial number of small entities so as to require a regulatory analysis. The regulation requires no new reports beyond those already now required. The analytical techniques approved here either can be handled by small facilities, or are widely available by contract at a reasonable price. Therefore, in accordance with 5 U.S.C. 605(b), I hereby certify that this rule will not have a significant adverse economic impact on a substantial number of small facilities.

(c) Under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*, the information provisions in this rule associated with the analytical test procedures equivalency program, 40

CFR 136.3 (a), (c) and (d), 136.4 and 136.5, and the sample preservation and holding times variances, 40 CFR 136.3(e), have been submitted to the Office of Management and Budget (OMB) as part of the final and interim-final rule published elsewhere in today's *Federal Register*. All approvals made on the final rule will be applicable to this proposed rule.

(Secs. 301, 304(h), 307 and 501(a), Pub. L. 95-217, 91 Stat. 1566, *et seq.* (33 U.S.C. 1251, *et seq.*) (the Federal Water Pollution Control Act Amendments of 1972 as amended by the Clean Water Act of 1977))

Dated: September 26, 1984.

William D. Ruckelshaus,
Administrator.

List of Subjects in 40 CFR Part 136

Water pollution control.

In consideration of the preceding, EPA proposes to amend Chapter I, Subchapter D of Title 40, Code of Federal Regulations, as follows:

Proposed Rule

For the reasons set out in the Preamble, it is proposed to amend Part 136, Chapter 1, Subchapter D of Title 40 of the Code of Federal Regulations as follows:

1. In § 136.3, Table IC is amended by renumbering to have 129 parameters, and by alphabetically inserting the following thirty-two new parameters: Acetone, Benzoic acid, Biphenyl, Carbazole, p-Cymene, n-Decane, Dibenzofuran, Dibenzothiophene, Diethyl ether, p-Dioxane, Diphenylamine, Diphenyl ether, 1,2-Diphenylhydrazine, n-Docosane, n-Dodecane, n-Eicosane, n-Hexacosane, n-Hexadecane, Hexanoic acid, Methyl ethyl ketone, β -Naphthylamine, n-Octacosane, n-Octadecane, α -Picoline, Styrene, α -Terpineol, n-Tetracosane, n-Tetradecane, n-Triacontane, 1,2,3-Trichlorobenzene, 2,3,6-Trichlorophenol, and 2,4,5-Trichlorophenol; by approving EPA Method 1624 for the analysis of Acetone, Diethyl ether, p-Dioxane, and Methyl ethyl ketone; by approving EPA Method 1625 for the analysis of Benzoic acid, Biphenyl, Carbazole, p-Cymene, n-Decane, Dibenzofuran, Dibenzothiophene, Diphenylamine, Diphenyl ether, 1,2-Diphenylhydrazine, n-Docosane, n-Dodecane, n-Eicosane, n-Hexacosane, n-Hexadecane, Hexanoic acid, β -Naphthylamine, n-Octacosane, n-Octadecane, α -Picoline, Styrene, α -Terpineol, n-Tetracosane, n-Tetradecane, n-Triacontane, 1,2,3-Trichlorobenzene, 2,3,6-Trichlorophenol, and 2,4,5-Trichlorophenol; by withdrawing approval of the following cited test procedures for the following

parameters: Benzidine, oxidation-colorimetric procedure, "Method for Benzidine and Its Salts in Wastewater", Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio (1976); and Carbon tetrachloride, Chlorobenzene, Chloroform, Methylene

chloride, PCB-1016, PCB-1221, PCB-1232, PCB-1242, PCB-1248, PCB-1260, Pentachlorophenol, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, 1,2,4-Trichlorobenzene and 1,1,2-Trichloroethane, gas chromatography, "Procedures for Pentachlorophenol, Chlorinated Organic Compounds, and

Pesticides", Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio (1976). As proposed to be revised, § 136.3, Table IC would read as follows:

§ 136.3 Identification of Test Procedures.

* * * * *

TABLE IC.—LIST OF APPROVED TEST PROCEDURES FOR ORGANIC COMPOUNDS

Parameter ¹	EPA method number ^{2, 7}			
	GC	GC/MS	HPLC	Other
1. Acenaphthene.....	610	625, 1625	610	
2. Acenaphthylene.....	610	625, 1625	610	
3. Acetone.....		1624		
4. Acrolein.....	603	* 624, 1624		
5. Acrylonitrile.....	603	* 624, 1624		
6. Anthracene.....	610	625, 1625	610	
7. Benzene.....	602	624, 1624		
8. Benzidine.....		* 625, 1625	605	
9. Benzo(a)anthracene.....	610	625, 1625	610	
10. Benzoic Acid.....		1625		
11. Benzo(a)pyrene.....	610	625, 1625	610	
12. Benzo(b)fluoranthene.....	610	625, 1625	610	
13. Benzo(g,h,i)perylene.....	610	625, 1625	610	
14. Benzo(k)fluoranthene.....	610	625, 1625	610	
15. Benzyl Chloride.....				Note 3, p. 130; Note 6, p. S102
16. Benzyl Butyl Phthalate.....	606	625, 1625		
17. Biphenyl.....		1625		
18. Bis(2-chloroethoxy) methane.....	611	625, 1625		
19. Bis(2-chloroethyl) ether.....	611	625, 1625		
20. Bis(2-ethylhexyl) phthalate.....	606	625, 1625		
21. Bromodichloromethane.....	601	624, 1624		
22. Bromoethane.....	601	624, 1624		
23. Bromoform.....	601	624, 1624		
24. 4-Bromophenylphenyl ether.....	611	625, 1625		
25. Carbazole.....		1625		
26. Carbon tetrachloride.....	601	624, 1624		
27. Chloroethane.....	601	624, 1624		
28. 4-Chloro-3-methylphenol.....	604	625, 1625		
29. Chlorobenzene.....	601, 602	624, 1624		
30. 2-Chloroethylvinyl ether.....	601	624, 1624		
31. Chloroform.....	601	624, 1624		
32. Chloromethane.....	601	624, 1624		
33. 2-Chloronaphthalene.....	612	625, 1625		
34. 2-Chlorophenol.....	604	625, 1625		
35. 4-Chlorophenylphenyl ether.....	611	625, 1625		
36. Chrysene.....	610	625, 1625	610	
37. p-Cymene.....		1625		
38. n-Decane.....		1625		
39. Dibenzo(a,h)anthracene.....	610	625, 1625	610	
40. Dibenzofuran.....		1625		
41. Dibenzothiophene.....		1625		
42. Dibromochlorobenzene.....	601	624, 1624		
43. 1,2-Dichlorobenzene.....	601, 602	624, 625		
	612	1625		
44. 1,3-Dichlorobenzene.....	601, 602	624, 625		
	612	1625		
45. 1,4-Dichlorobenzene.....	601, 602	624, 625		
	612	1625		
46. 3,3'-Dichlorobenzidine.....		625, 1625	605	
47. Dichlorodifluoromethane.....	601			
48. 1,1-Dichloroethane.....	601	624, 1624		
49. 1,2-Dichloroethane.....	601	624, 1624		
50. 1,1-Dichloroethene.....	601	624, 1624		
51. trans-1,2-Dichloroethene.....	601	624, 1624		
52. 2,4-Dichlorophenol.....	604	625, 1625		
53. 1,2-Dichloropropane.....	601	624, 1624		
54. cis-1,3-Dichloropropene.....	601	624, 1624		
55. trans-1,3-Dichloropropene.....	601	624, 1624		
56. Diethyl ether.....		1624		
57. Diethyl phthalate.....	606	625, 1625		
58. 2,4-Dimethylphenol.....	604	625, 1625		
59. Dimethyl phthalate.....	606	625, 1625		
60. Di-n-butyl phthalate.....	606	625, 1625		
61. Di-n-octyl phthalate.....	606	625, 1625		
62. 2,4-Dinitrophenol.....	604	625, 1625		
63. 2,4-Dinitrotoluene.....	609	625, 1625		
64. 2,6-Dinitrotoluene.....	609	625, 1625		
65. p-Dioxane.....		1624		
66. Diphenylamine.....		1625		
67. Diphenyl ether.....		1625		
68. 1,2-Diphenylhydrazine.....		1625		
69. n-Docosane.....		1625		
70. n-Dodecane.....		1625		
71. n-Eicosane.....		1625		
72. Epichlorohydrin.....				Note 3, p. 130; Note 6, p. S102.
73. Ethylbenzene.....	602	624, 1624		

TABLE IC.—LIST OF APPROVED TEST PROCEDURES FOR ORGANIC COMPOUNDS—Continued

Parameter ¹	EPA method number ²			
	GC	GC/MS	HPLC	Other
74. Fluoranthene.....	610	625, 1625	610	
75. Fluorene.....	610	625, 1625	610	
76. Hexachlorobenzene.....	612	625, 1625		
77. Hexachlorobutadiene.....	612	625, 1625		
78. Hexachlorocyclopentadiene.....	612	625, 1625		
79. Hexachloroethane.....	612	625, 1625		
80. n-Hexacosane.....		1625		
81. n-Hexadecane.....		1625		
82. Hexanoic acid.....		1625		
83. Ideno(1,2,3-cd)pyrene.....	610	625, 1625	610	
84. Isophorone.....	609	625, 1625		
85. Methylene Chloride.....	601	624, 1624		
86. 2-Methyl-4,6-Dinitrophenol.....	604	625, 1625		
87. Methyl ethyl ketone.....		1624		
88. Naphthalene.....	610	625, 1625		
89. β-Naphthylamine.....		1625		
90. Nitrobenzene.....	609	625, 1625		
91. 2-Nitrophenol.....	604	625, 1625		
92. 4-Nitrophenol.....	604	625, 1625		
93. N-Nitrosodimethylamine.....	607	625, 1625		
94. N-Nitrosodi-n-propylamine.....	607	625, 1625		
95. N-Nitrosodiphenylamine.....	607	624, 1625		
96. n-Octacosane.....		1625		
97. n-Octadecane.....		1625		
98. 2,2-oxybis(1-chloropropane).....	611	625, 1625		
99. PCB-1016.....	608	625		
100. PCB-1221.....	608	625		
101. PCB-1232.....	608	625		
102. PCB-1242.....	608	625		
103. PCB-1248.....	608	625		
104. PCB-1254.....	608	625		
105. PCB-1260.....	608	625		
106. Pentachlorophenol.....	604	625, 1625		
107. Phenanthrene.....	610	625, 1625	610	
108. Phenol.....	604	625, 1625		
109. α-Picoline.....		1625		
110. Pyrene.....	610	625, 1625	610	
111. Styrene.....		1625		
112. α-Terpineol.....		1625		
113. 2,3,7,8-Tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD).....		613		
114. 1,1,2,2-Tetrachloroethane.....	601	624, 1624		
115. Tetrachloroethene.....	601	624, 1624		
116. n-Tetracosane.....		1625		
117. n-Tetradecane.....		1624		
118. Toluene.....	602	625, 1624		
119. n-Triacontane.....		1625		
120. 1,2,3-Trichlorobenzene.....		1625		
121. 1,2,4-Trichlorobenzene.....	612	625, 1625		
122. 1,1,1-Trichloroethane.....	601	624, 1624		
123. 1,1,2-Trichloroethane.....	601	624, 1624		
124. Trichloroethene.....	601	624, 1624		
125. Trichlorofluoromethane.....	601	624		
126. 2,3,6-Trichlorophenol.....		1625		
127. 2,4,5-Trichlorophenol.....		1625		
128. 2,4,6-Trichlorophenol.....	604	625, 1625		
129. Vinyl Chloride.....	601	624, 1624		

¹ All parameters are expressed in micrograms per liter (μg/L).

² The full text of Methods 601-613, 624, 625, 1624, and 1625, are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit," of this Part 136.

³ Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978.

⁴ Method 624 may be extended to screen samples for Acrolein and Acrylonitrile. However, when they are known to be present, the preferred method for these two compounds are Method 603 or Method 1624.

⁵ Method 625 may be extended to include benzidine, hexachlorocyclopentadiene, N-nitrosodimethylamine, and N-nitrosodiphenylamine. However, when they are known to be present, Methods 605, 607, and 612, or Method 1625, are preferred methods for these compounds.

⁶ "Selected Analytical Methods Approved and Cited by the United States Environmental Protection," Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).

⁷ Each analyst must make an initial, one-time, demonstration of his ability to generate acceptable precision and accuracy with Methods 601-613, 624, 625, 1624, and 1625 (See Appendix A of this Part 136) in accordance with procedures given in section 8.2 of each of these Methods. Additionally, each laboratory, on an ongoing basis, must spike and analyze 10% (5% for Methods 624, 625, and 100% 1624, and 1625) of all samples to monitor and evaluate laboratory data quality in accordance with sections 8.3 and 8.4 of these Methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported for regulatory compliance purposes.

2. In § 136.3, Table ID is amended by withdrawing approval of the following cited test procedures for the following parameters: Aldrin, α-BHC γ-BHC (Lindane), Chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endrin, Heptachlor,

Heptachlor epoxide, and Toxaphene by the Gas Chromatography test procedures cited in, "Procedures for Pentachlorophenol, Chlorinated Organic Compounds, and Pesticides," Environmental Monitoring and Support Laboratory, U.S. Environmental

Protection Agency, Cincinnati, Ohio (1976). As proposed to be revised, § 136.3, Table ID would read as follows:

§ 136.3 Identification of Test Procedures.

* * * * *

TABLE ID.—LIST OF APPROVED TEST PROCEDURES FOR PESTICIDES ¹

Parameter	Method ²	EPA ^{3, 4}	Standard methods 15th Ed	ASTM	Other
1. Aldrin.....	GC.....	608			
	GC/MS.....	625			
2. Ametryn.....	GC.....				Note 3, p. 83; Note 6, p. S68.
3. Aminocarb.....	TLC.....				Note 3, p. 94; Note 6, p. S16.
4. Atratin.....	GC.....				Note 3, p. 83; Note 6, p. S68.
5. Atrazine.....	GC.....				Note 3, p. 83; Note 6, p. S68.
6. Azinphos methyl.....	GC.....				Note 3, p. 25; Note 6, p. S51.
7. Barban.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
8. α -BHC.....	GC.....	608			
	GC/MS.....	⁵ 625			
9. β -BHC.....	GC.....	608			
	GC/MS.....	625			
10. δ -BHC.....	GC.....	608			
	GC/MS.....	⁵ 625			
11. γ -BHC (Lindane).....	GC.....	608			
	GC/MS.....	625			
12. Captan.....	GC.....		509A		Note 3, p. 7.
13. Carbaryl.....	TLC.....				Note 3, p. 94; Note 6, p. S60.
14. Carbophenothion.....	GC.....				Note 4, p. 30; Note 6, p. S73.
15. Chlordane.....	GC.....	608			
	GC/MS.....	625			
16. Chloropropanol.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
17. 2,4'-D.....	GC.....		509B		Note 3, p. 115; Note 4, p. 35.
18. 4,4'-DDD.....	GC.....	608			
19. 4,4'-DDE.....	GC.....	608			
	GC/MS.....	625			
20. 4,4'-DDT.....	GC.....	608			
	GC/MS.....	625			
21. Demeton-O.....	GC.....				Note 3, p. 25; Note 6, p. S51.
22. Demeton-S.....	GC.....				Note 3, p. 25; Note 6, p. S51.
23. Diazinon.....	GC.....				Note 3, p. 25; Note 4, p. 30; Note 6, p. S51.
24. Dicamba.....	GC.....				Note 3, p. 115.
25. Dichlofenthion.....	GC.....				Note 4, p. 30; Note 6, p. S73.
26. Dichloran.....	GC.....		509A		Note 3, p. 7.
27. Dicofof.....	GC.....			D3086	
28. Dieldrin.....	GC.....	608			
29. Dioxathion.....	GC.....				Note 4, p. 30; Note 6, p. S73.
30. Disulfoton.....	GC.....				Note 3, p. 25; Note 6, p. S51.
31. Diuron.....	TLC.....				Note 3, p. 104.
32. Endosulfan I.....	GC.....	608			
	GC/MS.....	⁵ 625			
33. Endosulfan II.....	GC.....	608			
	GC/MS.....	⁵ 625			
34. Endosulfan sulfate.....	GC.....	608			
	GC/MS.....	625			
35. Endrin aldehyde.....	GC.....	608			
	GC/MS.....	625			
37. Ethion.....	GC.....				Note 4, p. 30.
38. Fenuron.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
39. Fenuron-TCA.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
40. Heptachlor.....	GC.....	608			
	GC/MS.....	625			
41. Heptachlor epoxide.....	GC.....	608			
	GC/MS.....	625			
42. Isodrin.....	GC.....				Note 4, p. 30; Note 6, p. S73.
43. Linuron.....	TLC.....				Note 3, p. 25; Note 6, p. S64.
44. Malathion.....	GC.....		509A		Note 3, p. 25; Note 4, p. 30; Note 6, p. S64.
45. Methiocarb.....	TLC.....				Note 3, p. 94; Note 6, p. S60.
46. Methoxychlor.....	GC.....		509A	D3086	Note 3, p. 7; Note 4, p. 30.
47. Mexacarbate.....	TLC.....				Note 3, p. 94; Note 6, p. S60.
48. Mirex.....	GC.....		509A		Note 3, p. 7.
49. Monuron.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
50. Monuron-TCA.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
51. Neburon.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
52. Parathion methyl.....	GC.....		509A		Note 3, p. 25; Note 4, p. 30.
53. Parathion ethyl.....	GC.....		509A		Note 3, p. 25.
54. PCNB.....	GC.....		509A		Note 3, p. 7.
55. Perthane.....	GC.....				Note 3, p. 83; Note 6, p. S68.
56. Prometon.....	GC.....				Note 3, p. 83; Note 6, p. S68.
57. Prometryn.....	GC.....				Note 3, p. 83; Note 6, p. S68.
58. Propazine.....	GC.....				Note 3, p. 83; Note 6, p. S68.
59. Propham.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
60. Propoxur.....	TLC.....				Note 3, p. 94; Note 6, p. S60.
61. Sebumeton.....	TLC.....				Note 3, p. 83; Note 6, p. S68.
62. Siduron.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
63. Simazine.....	GC.....				Note 3, p. 83; Note 6, p. S68.
64. Strobane.....	GC.....		509A		Note 3, p. 7.
65. Sweep.....	TLC.....				Note 3, p. 104; Note 6, p. S64.
66. 2,4,5-T.....	GC.....		509B		Note 3, p. 115; Note 4, p. 35.
67. 2,4,5-TP (Silvex).....	GC.....		509B		Note 3, p. 115.
68. Terbutylazine.....	GC.....				Note 3, p. 83; Note 6, p. S68 69.
69. Toxaphene.....	GC.....	608			
	GC/MS.....	625			
70. Trifluralin.....	GC.....		509A		Note 3, p. 7.

¹ Pesticides are listed in this table by common name for the convenience of the reader. Additional pesticides may be found under Table IC, where entries are listed by chemical name.

² The full text of Methods 608 and 625, are given at Appendix A, "Test Procedures for Analysis of Organic Pollutants," of this Part 136. The standardized test procedure to be used to determine the method detection limit (MDL) for these test procedures is given at Appendix B, "Definition and Procedure for the Determination of the Method Detection Limit", of this Part 136.

³ Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, September, 1978. This EPA publication includes thin-layer chromatography (TLC) methods.

* "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey, Techniques of Water-Resources Investigations, Book 5, Chapter A3 (1972).

* The method may be extended to include α -BHC, δ -BHC, endosulfan I, endosulfan II, and endrin. However, when they are known to exist, Method 608 is the preferred method.

* "Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency," Supplement to the Fifteenth Edition of *Standard Methods for the Examination of Water and Wastewater* (1981).

⁷ Each analyst must make an initial, one-time, demonstration of his ability to generate acceptable precision and accuracy with Methods 608, and 625 (See Appendix A of this Part 136), in accordance with procedures given in Section 8.2 of each of these methods. Additionally, each laboratory, on an ongoing basis, must spike and analyze 10% of all samples analyzed with Method 608 or 5% of all samples analyzed with Method 625 to monitor and evaluate laboratory data quality in accordance with Sections 8.3 and 8.4 of these methods. When the recovery of any parameter falls outside the warning limits, the analytical results for that parameter in the unspiked sample are suspect and cannot be reported for regulatory compliance purposes.

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