ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 86

[FRL 1360-4]

Revised Motor Vehicle Exhaust Emission Standards for Carbon Monoxide (CO) for 1981 and 1982 Model Year Light-Duty Vehicles

AGENCY: Environmental Protection Agency.

ACTION: Final rule.

SUMMARY: This regulation establishes CO emission standards for 1981 model year light-duty vehicles belonging to certain engine families for which I have granted waivers from the standard otherwise applicable under section 202(b)(5) of the Clean Air Act, 42 U.S.C. 7521(b)(5).

EFFECTIVE DATE: December 10, 1979.

ADDRESS: Information relevant to this rule is contained in Public Docket EN-79-17 at the Central Docket Section of the Environmental Protection Agency (EPA), Room 2903B, 401 M Street, SW., Washington, D.C. 20460 and are available for review between the hours of 8:00 a.m. and 4:00 p.m. As provided in 40 CFR Part 2, a reasonable fee may be charged for copying services.

FOR FURTHER INFORMATION CONTACT: Glenn Unterberger, Manufacturers Operations Division (EN-340), U.S. Environmental Protection Agency, 401 M Street, SW., Washington, D.C. 20460, (202) 472-9417.

SUPPLEMENTARY INFORMATION: Section 202(b)(1)(A) of the Clean Air Act ("the Act"), 42 U.S.C. 7521(b)(1)(A), requires that regulations applicable to CO emissions from light-duty vehicles or engines manufactured during or after the 1981 model year shall contain standards which require a reduction of at least 90 percent from CO emission levels allowable under the 1970 model year standards. Regulations implementing this requirement have established a CO standard, often referred to as the statutory standard for CO, of 3.4 grams per vehicle mile (gpm).

Section 202(b)(5) of the Act authorizes the Administrator, on application of any manufacturer, to waive the statutory CO standard for the 1981 and 1982 model years for any light-duty vehicle model regarding which the Administrator can make certain findings. In these cases, the Act requires that I promulgate substitute CO standards for 1981 and 1982 model year light-duty vehicles as discussed below. Applications for these waivers were submitted by Fuji Heavy Industries, Ltd., Nissan Motor Co., Ltd., Regie Nationale des Usines Renault, and Toyo Kogyo Co., Ltd. The statutory criteria, my determinations regarding the criteria with respect to the vehicle models covered by the waiver applications, and my decisions to grant or deny the waiver applications appear in the consolidated decision published above. In that decision, I granted waivers covering the following vehicle models (engine families for purposes of that decision) for the 1981 model year only:

Manufacturer	Engine family
Toyo Kogyo Co., Ltd	91 CID, 120 CID

Once I have decided to grant waiver applications for these two 1981 model year vehicle models, the Act requires that I simultaneously promulgate regulations adopting emission standards not permitting CO emissions from 1981 model year vehicles of these two Toyo Kogyo models to exceed 7.0 gpm. Moreover, that Act further requires that I promulgate regulations establishing these standards no later than 60 days after I receive the waiver application in question.[1] The public has received an opportunity to comment on the waiver applications at issue, and I have considered those comments in making the consolidated decision which requires the promulgation of this rule. For these reasons, I find that providing notice and an opportunity to comment on this rulemaking before final promulgation is impracticable and unnecessary.

Note.—The Environmental Protection Agency has determined that this document does not contain a major proposal requiring preparation of an economic impact analysis under Executive Orders 11821 and 11944 and OMB Circular A-107.

In addition, because the decision already accompanying this rulemaking contains a detailed analysis indicating that this rulemaking will have a negligible effect on air quality, the Environmental Protection Agency has not prepared an Environmental Impact Statement to accompany this rulemaking as well.

Dated: November 8, 1979.

Douglas M. Costle,

Administrator.

40 CFR Part 86 is amended as follows:

Subpart A—General Provisions for Emission Regulations for 1977 and Later Model Year New Light-Duty Vehicles, 1977 and Later Model Year New Light-Duty Trucks and 1977 and Later Model Year New Heavy-Duty Engines.

40 CFR 86.081-8(a)(1), published at 44 FR 53408 (September 13, 1979), is revised to read as follows:

§ 86.081-8 Emissions standards for 1981 and later model year light-duty vehicles.

(a)(1) Exhaust emissions from 1981 and later model year light-duty vehicles shall not exceed the following levels for the following pollutants:

(i) Hydrocarbons—0.41 grams per vehicles mile;

(ii) Carbon monoxide—3.4 grams per vehicle mile, except that

(A) Carbon monoxide emissions from light-duty vehicles of the following 1981 and 1982 model year engine families shall not exceed 7.0 grams per vehicle mile:

Manufacturer	Engine Family
American Motors Corporation	258 CID
BL Cars, Ltd	TR8, XJ12
Chrysler Corporation	1.7 liter, 3.7 liter, 5.2 liter/4-V
General Motors Corporation	2.8 liter/173 CID-2V, 3.8 liter/231 CID-2V
Toyota Motor Company, Ltd	88.6 CID

(B) Carbon monoxide emissions from light-duty vehicles of the following 1981 model year engine families shall not exceed 7.0 grams per vehicle mile:

Manufacturer	Engine family
Toyo Kogyo Company, Ltd	91 CID, 120 CID

(iii) Oxides of nitrogen—1.0 grams per vehicle mile except that oxides of nitrogen emissions from 1981 and 1982 model year light-duty vehicles manufactured by American Motors Corporation shall not exceed 2.0 grams per vehicle mile.

(Secs. 202 and 301(a), Clean Air Act, as amended, (42 U.S.C. 7521 and 7601(a)))

[FR Doc. 79-36529 Filed 11-30-79; 8:45 am]

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[1] In this case, both Toyo Kogyo Co., Ltd., and Nissan Motor Co., Ltd., have consented to brief extensions of the period within which I was to decide on their respective waiver applications.

ENVIRONMENTAL PROTECTION AGENCY

[FRL 1360-4]

Applications for Waiver of Effective Date of the 1981 Model Year Carbon Monoxide Emission Standard for Light-duty Motor Vehicles—Second Consolidated Decision of the Administrator

I. Introduction

This is the second consolidated decision I have issued under Section 202(b)(5) of the Clean Air Act as amended (Act), 42 U.S.C. 7521(b)(5), regarding applications from automobile manufacturers for waiver of the 3.4 grams per vehicle mile (gpm) carbon monoxide (CO) emission standard scheduled to apply to 1981 and 1982 model year light-duty motor vehicles and engines.[1]

As the introduction to the first consolidated decision explains, Section 202(b)(1)(A) of the Act establishes the standards applicable to CO emissions for 1977 and later model year light-duty motor vehicles and engines. This section, included in the 1977 amendments to the Act, requires the Administrator of the Environmental Protection Agency (EPA) to promulgate regulations providing that CO emissions for 1977 through 1979 vehicles may not exceed 15.0 gpm. For 1980 model year vehicles, this section requires a standard which does not permit CO emissions to exceed 7.0 gpm. Beginning in model year 1981, this section mandates standards which require a reduction in CO emissions of at least 90 percent from the CO standard applicable to 1970 model year vehicles.

As Administrator, I promulgated regulations which set the CO standard for 1981 and later model year vehicles at 3.4 gpm.[2]

The 1977 amendments to the Act, however, also included a provision allowing the Administrator, under certain limited conditions, to delay implementation of the 3.4 gpm CO standard. Specifically, Section 202(b)(5) of the Act provides that any light-duty motor vehicle or engine manufacturer may apply for waiver of the 3.4 gpm CO standard for any of its 1981 or 1982 model year vehicle or engine models. This section directs the Administrator to make a determination on each application within 60 days from receipt of the application. Should the Administrator decide to grant a waiver for a model, he simultaneously must promulgate standards which do not allow CO emissions over 7.0 gpm for those models covered by the granted waiver applications.

Section 202(b)(5)(C) of the Act provides in pertinent part the following:

> The Administrator may grant such waiver if he finds that protection of the public health does not require attainment of such 90 percent reduction for carbon monoxide for the model years to which such waiver applies in the case of such vehicles and engines and if he determines that—
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> (i) such waiver is essential to the public interest or the public health and welfare of the United States;
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> (ii) All good faith efforts have been made to meet the standards established by this subsection;
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> (iii) The applicant has established that effective control technology, processes, operating methods, or other alternatives are not available or have not been available with respect to the model in question for a sufficient period of time to achieve compliance prior to the effective date of such standards, taking into consideration costs, driveability, and fuel economy; and
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> (iv) Studies and investigations of the National Academy of Sciences conducted pursuant to subsection (c) and other information available to him has not indicated that technology, processes, or other alternatives are available (within the meaning of clause (iii)) to meet such standards.

Congress first set statutory emission standards for hydrocarbon (HC) and CO emissions from light-duty motor vehicles and engines in the 1970 amendments to the Act.[3] Section 202(b)(1) of that version of the Act required that HC and CO emission standards for 1975 and later model year vehicles represent at least a 90 percent reduction from HC and CO standards in effect in model year 1970. Section 202(b)(5) of that version of the Act, however, authorized the Administrator, upon application of a manufacturer, to suspend for one year the effective date of those emission standards with respect to that applicant.[4]

The criteria for granting a suspension request were essentially the same as those provided in the current section 202(b)(5)(C) waiver provision, with two exceptions. The 1970 version of the Act did not explicity require the Administrator either to assess the effect of the suspension on public health or to take into consideration costs, driveability, and fuel economy in evaluating available technology.

In early 1972, the Administrator received suspension applications from five automobile manufacturers. The Administrator initially denied all five applications in a decision issued on May 12, 1972.[5] In that decision, he determined that no applicant had demonstrated that requisite technology was not available to enable compliance with the statutory HC and CO standards. On appeal, the reviewing court ultimately decided to remand the record to the Administrator to reconsider his determination regarding available technology.[6] On remand, the Administrator reversed his decision and granted to all manufacturers a one-year suspension of the statutory HC and CO standards until the 1976 model year.[7] He based his reversal on the conclusion that the risk of an errant denial of the suspension requests (which might result in severe economic disruption) outweighed the risk of an errant grant (which might result in environmental benefits not achieved). The Administrator was particularly concerned about the economic impact of any unanticipated production problems that could occur when manufacturers first began using catalytic converters in production in order to meet the statutory HC and CO standards.

In the 1974 amendments to the Act, Congress further postponed the effective date of these statutory standards until the 1977 model year, and authorized the Administrator to suspend that effective date until the 1978 model year under the same criteria set forth in the 1970 version of the Act.[8] After receiving suspension applications from five manufacturers in early 1975, the Administrator issued a decision granting the applications.[9]

In that decision, the Administrator concluded that the requisite technology for meeting the statutory emission standards was generally available to the industry. He further determined, however, that unregulated sulfuric acid emissions resulting from use of the requisite technology presented a significant risk to public health. The Administrator concluded that this risk outweighed any environmental savings achieved by denying the applications,

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[1] The first consolidated decision is published at 44 FR 53376 (September 13, 1979).

[2] 40 CFR 86.081-8(a)(1)(ii), 44 FR 47884 (August 15, 1979) (revising 43 FR 37972 (August 24, 1978)).

[3] Clean Air Amendments of 1970, Pub. L. No. 91-604, section 6, 81 Stat. 499 (1970) (current version at 42 U.S.C. 7521(b)(1)).

[4] This contrasts with the current section 202(b)(5), which requires the Administrator to make a separate waiver determination for each model covered by an application.

[5] In re: Applications for Suspension of 1975 Motor Vehicle Exhaust Emission Standards, Decision of the Administrator (May 12, 1972).

[6] *International Harvester Co.* v. *Ruckelshaus*, 478 F.2d 655 (D.C. Cir. 1973).

[7] 38 FR 1017 (April 26, 1973).

[8] Energy Supply and Environmental Coordination Act of 1974, Pub. L. No. 93-319, 88 Stat. 246 (1974) (current version at 42 U.S.C. 7521).

[9] 40 FR 1190 (March 14, 1975).

and therefore justified suspension of the statutory standards for HC and CO until the 1978 model year. Before the beginning of that model year, Congress enacted the 1977 amendments to the Act, which set forth the current schedule for implementing (or waiving) the CO emission standards.

Congress intended that any waivers granted under the 1977 amendments be narrow in scope and not apply to the entire industry. While the Act previously directed the Administrator to consider applications for delay of the effective date of statutory emission standards on a manufacturer-by-manufacturer basis, the current section 202(b)(5) requires the Administrator to consider separate waiver applications for each vehicle model at issue.

Requiring the Administrator to make individual determinations for small portions of the total vehicle population indicates that Congress wanted any relaxation of the statutory 90 percent reduction requirement for CO to be applied, where appropriate, as narrowly and precisely as practicable. Indeed, discussion in Congress on the Act's current CO waiver provision include the explicit statement that "[t]he waiver is not a general waiver for all manufacturers, nor is it a general waiver for all models of vehicles produced by a single manufacturer."[10] Instead, the waiver provision is to be available for a particular model line of a manufacturer which cannot meet the 3.4 gpm standard across the board in the 1981 model year.[11]

On October 13, 1978, EPA published "Guidelines for Applications for Waiver of the 1981 Carbon Monoxide Emission Standard."[12] These guidelines outlined the information which EPA sought from waiver applicants and directed applicants to submit a separate application for each vehicle model for which a waiver is sought. For purposes of these proceedings, the guidelines defined "model" as synonymous with the term "engine family" as defined in 40 CR 86.077-2 and 86.078-24(a)(2) through (a)(4)(1977).

From July 9 to July 12, 1979, EPA held a public hearing to consider waiver applications the Agency had received up until that time. The waiver applications under consideration at that hearing were submitted by American Motors Corporation, BL Cars, Ltd., Chrysler Corporation, General Motors Corporation, Toyota Motor Co., Ltd., and Volkswagen AG. EPA received testimony from the waiver applicants, from other automobile manufacturers which at that time had not filed for a waiver, and from suppliers and developers of emission control systems and components.[13]

Consistent with the requirement of section 202(b)(5)(A) of the Act, I made a separate determination for each engine family for which one of the six manufacturers had requested a waiver. This set of determinations was published as a consolidated decision.[14] In that decision, I indicated that I was denying the waiver applications covering those engine families for which I had determined, for either one of two reasons, that the applicant had failed to meet the statutory criterion in section 202(b)(5)(C)(iii) of the Act. Specifically, I denied some of the waiver applications because I determined that effective control technology[15] was available to permit the engine families in question to meet the 3.4 gpm CO standard in the 1981 model year, even after considering costs, driveability, and fuel economy. I denied other waiver applications because the applicant had failed to provide sufficient information to establish that such technology was not available for the engine families in question. I granted the waiver applications covering the remaining engine families, for which I was able to determine that the requisite technology was not available, because those waiver applications also met each of the remaining statutory criteria for receiving a waiver.

EPA held another public hearing on September 12, 1979, to consider waiver applications it had reviewed since the July 9–12 hearing. At this hearing, EPA reviewed waiver applications in order of their receipt from Toyo Kogyo Co., Ltd. (hereinafter "Toyo Kogyo"), Nissan Motor Co., Ltd. (Nissan), and Fuji Heavy Industries, Ltd. (Fuji), covering all the engine families scheduled for production by each of these manufacturers, and from Regie Nationale des Usines Renault (Renault), covering one of its engine families.[16]

As with the first consolidated decision, I have made a separate determination for each engine family covered by a waiver request[17] and have consolidated these separate determinations into this decision.

II. Summary of Decision

I have decided to deny all but two of the waiver applications under consideration in this consolidated decision and to grant those two waiver requests specified below. I have reached this set of determinations by employing the same general evaluation process I used in the first consolidated decision. Much of the rationale which applied in that decision is controlling here as well. A more detailed discussion of the basis for this second consolidated decision follows this summary.

In order to grant a waiver for an engine family, I must determine that an applicant has met each criterion specified by the Act. For two Toyo Kogyo engine families covered by waiver applications, I have determined that Toyo Kogyo has met each of the statutory criteria for receiving the waiver for the 1981 model year. I also have determined, however, that those two engine families can incorporate effective control technology, considering costs, driveability, and fuel economy, to meet the 3.4 gpm CO standard by the 1982 model year. As a

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[10] 123 Cong. Rec. S 13703 (daily ed. Aug. 4, 1977) (remarks of Sen. Muskie).

[11] Id. at S 13702–13703.

[12] 43 FR 47272 (1978).

[13] Testimony received at that hearing, as well as all other information considered in deciding on that group of waiver applications, is included in EPA Public Docket EN–79–4.

[14] See note 1, supra.

[15] As was the case in the first consolidated decision, I am using the term "technology" in this decision to encompass the statutory language "technology, processes, operating methods, or other alternatives" included as part of section 202(b)(5)(c)(iii) of the Act.

[16] This decision uses the following abbreviated citations:

Fuji App.—Fuji Heavy Industries. Ltd., Waiver Request of Carbon Monoxide Standard for 1981 and 1982 Model Year Light-Duty Vehicles, dated September, 1979.

N App.—Nissan Motor Co., Ltd., Application for Waiver of the 1981 and 1982 CO Emission Standard for Light Duty Vehicles, dated August, 1979.

R App.—Regie National des Usines Renault Application for Waiver of 1981 and 1982 Carbon Monoxide Emission Standard, dated September, 1979.

TK App.—Toyo Kogyo Co., Ltd., Application for Waiver of 1981 and 1982 CO Emission Standard for Passenger Cars, dated July, 1979.

Sept. 12 Tr.—The transcript of the public hearings held on September 12, 1979, on these waiver applications.

Citations used here for waiver applications considered under the first consolidated decision are the same as those listed at 44 FR 53377, note 12 (September 13, 1979). Other submissions are cited by the name or initials of the submitting party and the date on the submission, e.g. TK 9/28/79 p.1.

[17] Strictly speaking, I have made separate determinations here for each engine displacement, rather than for each engine family, covered by a manufacturer's set of waiver requests. Because so many different engine families can be associated with a single engine displacement of a given waiver applicant, it is impracticable for me to make a separate waiver determination for each of those engine families. By avoiding a strict engine family-by-engine family approach, I can avoid placing narrow limits on the type of vehicle design a manufacturer may choose to use; instead, I am providing the manufacturer the opportunity to use whatever design it deems best suited to enable a given engine with a given displacement to meet the emission standards established for it. Thus, as was the case in the first consolidated CO waiver decision, the term "engine family" as used in this decision actually describe a broader class of vehicles than it normally would under the definition established by 40 CFR Part 86.

result, I am granting waivers which cover only 1981 model year vehicles of these two engine families.

As I did in the first consolidated decision, I have based my decision here to deny waiver requests for the other engine families at issue on either of two determinations. For some of those engine families, I have determined that those families can incorporate effective control technology, considering costs, driveability, and fuel economy, to meet the 1981 model year statutory 3.4 gpm CO standard. For the remainder of those engine families not receiving waivers, I have determined that the applicant has failed to provide sufficient information to establish that such technology is not available.

A. Waiver Applications Granted

The waiver applications which I have decided to grant cover 1981 model year vehicles of the following engine families:

Waiver Applications Granted

Manufacturer	Engine family
Toyo Kogyo Company, Ltd.	91 CID (1981 model year only).
	120 CID (1981 model year only).

As discussed more fully below, I have concluded that technology will not be available for incorporation into 1981 model year vehicles of these particular engine families to enable these families to meet a 3.4 gpm CO standard. I am prescribing interim CO emission standards of 7.0 gpm for the 1981 model year for each of the engine families receiving waivers. The statutory 3.4 gpm CO standard will apply to 1982 model year vehicles of these two engine families, however, because I have determined that technology, considering cost, driveability, and fuel economy, will be available by the 1982 model year to enable these engine families to meet the 3.4 gpm CO standard.

In making determinations for these engine families, I have not considered whether these two engine families would be capable of meeting the 3.4 gpm CO standard by replacing their catalysts during their useful life. Such replacement depends on vehicle owners taking affirmative action for which significant disincentives exist. Because many owners are unlikely to replace their vehicles' catalysts, I have determined generally that effective CO control technology within the meaning of the Act is not available for engine families otherwise unable to meet the 1981 statutory emission requirements for CO.

Protection of the public health does not require attainment of the 3.4 gpm CO standard in the 1981 model year by the engine families for which I have granted waivers. The effect on ambient air quality which would result from allowing the two Toyo Kogyo engine families receiving waivers to meet a CO standard of 7.0 gpm for the 1981 model year is insignificant. As a result, the impact these waivers would have on any state's ability to meet the National Ambient Air Quality Standards (NAAQS) for CO (in other words, the state's ability to achieve CO levels recognized as protective of public health) also would be insignificant.

I have determined the two waivers which I have granted to be essential to the public interest. By granting these waivers, I will permit Toyo Kogyo to market one or more engine families which they otherwise may not have been allowed to market, or may only have been allowed to market with the requirement of an expensive catalyst change. These waivers are essential to the public's interest in maintaining a diversified and competitive automotive industry for the United States market.

Specifically, these waivers enable Toyo Kogyo to continue selling two of its three engine families without requiring catalyst changes. Granting waivers to ensure the viability of this applicant serves the public interest by helping to preserve the level of competition that currently exists in the automotive industry.

Each of the waiver applicants contended that it has acted in good faith in trying to meet the 3.4 gpm standard. In general, information in the record supplies support for determining that the applicants have met the Act's good faith criterion. In some limited instances, though, the applicants' respective showings in this regard are at best marginal. Nevertheless, in the absence at this time of any evidence supporting a contrary conclusion (even for the marginal showings), I have determined that each of the applicants, including Toyo Kogyo, has met the good faith criterion for those engine families for which I have granted a waiver.

Review of studies and investigations of the National Academy of Sciences (NAS) and other information available to me has not indicated that the requisite technology, considering costs, driveability, and fuel economy, is available for these engine families. Available NAS studies only address the issue of whether technology is available in general without considering the issue of availability in the context of the details associated with a particular engine family. The NAS is in the process of preparing a new study on the availability of effective CO control technology.

Other information has been obtained from non-applicant manufacturers or part suppliers and developers by subpoena, or from sources not directly associated with proceedings on these waiver applications and has been included in the record for the determinations on these applications. This information does not indicate that the requisite technology, considering costs, driveability, and fuel economy, will be available for the engine families receiving a waiver for the 1981 model year.

Therefore, concurrently with this consolidated decision I am promulgating regulations establishing a 7.0 gpm CO emission standard for 1981 model year vehicles of the two engine families I have listed.

B. Waiver Applications Denied

As stated earlier, I am denying those waiver applications which apply to the remaining engine families as follows:

Waiver Applications Denied

Manufacturer	Engine family
Fuji	97 CID.
	109 CID.
Nissan	75 CID.
	85/91 CID.[18]
	119 CID.
	146/168 CID.[19]
	EF-A.[20]
	EF-B.
Renault	85 CID.
Toyo Kogyo	70 CID (Rotary).
	91 CID (1982 model year only).
	120 CID (1982 model year only).

I cannot conclude that effective control technology, considering costs, driveability, and fuel economy, is not available to enable those engine families to meet the statutory CO standard in the 1981 model year.

Nissan submitted emission test data which indicated that its 119 CID engine family can meet the 3.4 gpm CO standard by using a design Nissan has considered for that engine family. Nissan's 75, 85/91, and 146/168 CID engine families will be capable of attaining the 3.4 gpm CO standard in the 1981 model year by adding one or more available features to the design of the engine family. Toyo Kogyo's 91 and 120 CID engine families also will be capable of attaining the 3.4 gpm CO standard in the 1982 model year by adding available features which will become available by that time.

For the remaining engine families covered by waiver applications which I

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[18] In its certification program, EPA historically has treated the Nissan engines of these two sizes as part of the same engine family in certification.

[19] Id.

[20] Nissan has requested confidentiality for descriptions of two of its engine families; thus, I am using the fictitious designations "EF-A" and "EF-B" to represent these families.

have denied, the applicants have failed to establish that effective CO control technology will not be available to them. The waiver applications for Fugi's 97 and 109 CID engine families and for Renault's 85 CID engine family, respectively, have failed to establish that size limitations prevent the incorporation of effective emission control equipment into vehicles of these engine families. Toyo Kogyo's 70 CID engine family using a thermal reactor and no catalyst is not susceptible to this decision's normal, rigorous analysis of emissions performance capabilities; however, the only emission test data available on that family indicate that the family can meet the 3.4 gpm CO standard. Nissan failed to submit emission test results which provide an adequate basis for me to determine that its engine families "A" and "B" are not capable of attaining the 3.4 gpm CO standard.

Considerations of costs, driveability, or fuel economy, whether viewed separately or cumulatively, do not give me a basis for altering my determinations regarding the availability of technology for these engine families which have been denied waivers. The extra costs associated with implementing technology capable of meeting the 3.4 gpm standard for those engine families, while not necessarily insignificant, are not substantial enough compared to the costs of meeting a standard no higher than 7.0 gpm to justify a conclusion that use of that technology is not feasible. The higher prices which manufacturers will need to charge to cover these extra costs will not be so large as to threaten the capabilities of these engine families to achieve or maintain a competitive position in the marketplace by making vehicles of the engine families in question unacceptable to consumers. I have determined, therefore, that these costs do not prevent the requisite control technology from being reasonably available to enable these engine families to achieve the 90% reduction in CO emissions which the Act establishes as an ultimate target for light-duty motor vehicles.

Furthermore, no waiver applicant has presented information which indicates that implementing technology capable of achieving the 3.4 gpm standard would have a sufficient adverse effect on driveability, relative to the driveability levels which an applicant reasonably could attain in conjunction with a standard not exceeding 7.0 gpm, to make the vehicles in question unacceptable to consumers. Nor has any waiver applicant demonstrated that implementation of that technology either will prevent the engine families in question from meeting Federal fuel economy requirements or will cause an unreasonable fuel economy penalty relative to fuel economy levels achievable in conjunction with a standard not exceeding 7.0 gpm.

Thus, while these remaining engine families may meet some, or all, of the remaining statutory criteria for receiving waivers, my determinations regarding available technology, considering costs, driveability, and fuel economy, preclude me from granting waivers covering these engine families.

III. Discussion

A. Methodology for Assessing Available Technology

As was the case under the first consolidated CO waiver decision, a key question I must face in reviewing this set of waiver applications is whether technology is available to enable an engine family covered by a waiver application to meet the 3.4 gpm CO standard in the 1981 model year. Sections 202(b)(5)(C) (iii) and (iv) of the Act indicate that Congress intended all vehicles to comply with the Act's 90 percent CO emission reduction requirement where practicable. Section 202(b)(5)(C)(iii) of the Act expressly assigns an applicant the task of establishing that effective CO control technology is not available, taking into consideration costs, driveability, and fuel economy. Even if the Administrator determines that an applicant has met this burden, section 202(b)(5)(C)(iv) requires the Administrator to make sure before he may grant a waiver request that other available information does not contradict the applicant's position on available technology.

1. *Applicants' Positions Summarized.* Each automobile manufacturer has reached a state in its development of CO emission controls at which it has narrowed the range of strategies it contemplates employing to meet the 3.4 gpm standard to, at most, a few alternative systems. To support contentions that effective control technology is not available within the meaning of the Act, the waiver applicants have provided both descriptions of the systems they have been considering in trying to attain the 3.4 gpm CO emission standard and emission test results they have measured from vehicles incorporating those systems. Each application proposed that I grant the requested waivers to cover engine families produced in both the 1981 and 1982 model years and that a 7.0 gpm CO standard apply to those families.

a. *Fuji Heavy Industries, Ltd.* Fuji asserted that it has not yet been able to develop technology capable of complying with all aspects of a 3.4 gpm CO standard by the 1981 model year without employing a catalyst change during the first 50,000 miles of vehicle operation.[21] Fuji pointed out that its 1% U.S. market share was small enough that granting waivers for those vehicles would have little significant effect on ambient air quality and public health.[22] Fuji also stated that the requested waivers would serve a significant role in promoting diversity and competition within the industry, since four-wheel drive, multipurpose vehicles constitute one-half of its U.S. sales.[23]

b. *Nissan Motor Co., Ltd.* Nissan stated that although its efforts in CO emission control have produced promising results, it has not yet been able to demonstrate that it can comply with all the requirements associated with a 3.4 gpm CO standard in the 1981 model year.[24] Moreover, Nissan claimed that it had insufficient lead time to conduct necessary durability and reliability testing on its systems before its 1981 model year decision deadlines.[25] Nissan asserted that granting waivers would permit a $60–$110 reduction in the cost of its vehicles and have a negligible effect on public health.[26]

c. *Regie Nationale des Usines Renault.* Renault applied for a waiver for only one of its two engine families. Renault asserted that the structure of its 85 CID Le Car model (designed in 1966–1970) does not permit the adaptation of an emission control system to meet 3.4 gpm CO and 1.0 gpm oxides of nitrogen (NO_x) standards within the remaining lead time available for the 1981 model year.[27] Renault pointed out that sales of Le Car constitute only 0.1% of the U.S. market and therefore would not contribute to deterioration in air quality or adversely affect public health if produced to meet a less stringent CO standard.[28] Moreover, Renault maintained that granting a waiver for Le Car vehicles would permit it to market a

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[21] F. App., p. 1-3.

[22] Id.; Sept. 12 Tr. at 103–104.

[23] Sept. 12 Tr. at 104.

[24] Sept. 12 Tr., p. 53. N. App., p. 102.

[25] N. App., p. 5.5.1.

[26] N. App., p. 3.1.

[27] Sept. 12 Tr., p. 161; R. App., p. I/1. Renault stated that its own development efforts to meet those two emission standards were unsuccessful in meeting established design targets. Sept. 12 Tr., pp. 163, 164. Moreover, Renault indicated that introducing purchased technology into production for this engine family would require a two-year lead time. Sept. 12 Tr., p. 165.

[28] R. App., p. I/1.

standard "50-state" vehicle that would comply nationwide with the more stringent NO_x emission and allowable maintenance requirements effective in California.[29]

d. *Toyo Kogyo Co., Ltd.* Toyo Kogyo filed waiver applications for two engine families using conventional piston engines and one engine family using a rotary engine. Toyo Kogyo stated that the system it planned to use for the rotary engine family would involve a $40 cost penalty and a 5% fuel economy penalty at a 3.4 gpm CO standard relative to the system it would use to meet a 7.0 gpm CO standard.[30] The alternative systems Toyo Kogyo is thinking of using for its conventional engine families assertedly either involve cost or fuel economy penalties ($50 and 5%) or have not adequately demonstrated an ability to meet the 3.4 gpm standard.[31] Toyo Kogyo claimed that some refinements in both the rotary and conventional systems would be necessary before those systems could be put to practical use in meeting a 3.4 gpm CO standard.[32]

2. *Decision Methodology.* Appendix A to this consolidated decision contains an assessment of technology available to meet the 3.4 gpm CO standard for each engine family in question. These assessments result from a review of the information contained in the waiver applications on these systems and of other information contained in the public record for this consolidated decision.

Appendix A evaluates the availability of effective control technology in the same way that Appendix A of the first consolidated CO waiver decision did.[33] Specifically, Appendix A to this decision assesses the emissions performance of each engine family as described in the waiver application and also of each described engine family after hypothetically factoring in one or more system improvements through the use of "adjustment factors". The adjustment factors account for only those emission control features (such as an additional catalyst, air injection, or increased catalyst noble metal loadings) which 1) are reasonably available to a manufacturer for incorporation into a 1981 or 1982 model year engine family's design in order to achieve greater reduction of CO emissions and 2) have their respective effects on emissions reflected in data which are available to me.[34]

Appendix A employs methodology which applies these few carefully selected adjustment factors to emission test results supplied by a waiver applicant. This allows me to ascertain not only what CO emission levels the systems as described in the waiver applications can attain but also what these systems could attain had the systems incorporated "state-of-the-art" technology in which a high level of confidence can be placed.[35] EPA's Administrator also has used this approach in assessing technology in conjunction with past decisions on applications for suspension of statutory motor vehicle exhaust emission standards.[36]

Appendix A then addresses whether the engine family under each scenario is capable of "certifying" (passing EPA's certification testing requirements) [37] with 0.41 gpm HC, 3.4 gpm CO, and 1.0 gpm NO_x standards in effect.[38] Consistent with the methodology used in the previous suspension decisions and outlined in the waiver application guidelines,[39] Appendix A contains this evaluation for each engine family for which sufficient emission test data were available by using a "Monte Carlo" statistical simulation technique. The Monte Carlo technique employs emission test data provided for a vehicle of a given engine family to generate the emission level distributions that would be expected to occur for a large fleet of durability vehicles of that engine family as measured by certification testing.[40] Appendix A assigns a "pass" or "fail" determination to each engine family scenario according to whether the applicable Monte Carlo simulation indicated that more or less than 80% of the vehicles of the engine family in question could meet certification testing requirements for each regulated pollutant if each were tested once.[41] In this manner the methodology takes into

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[29] R. App., p. 1/2.

[30] TK App., p. 1.2.

[31] Id. at pp. 1.2–1.3.

[32] Sept. 12 Tr., p. 11–14.

[33] See In re: Applications for Waiver of Effective Date of the 1981 Model Year Carbon Monoxide Emission Standard for Light-Duty Vehicles, Consolidated Decision of the Administrator, 44 FR 53376, 53389–53402 (September 13, 1979). Appendix A of the first consolidated decision included an examination of the potential emissions performance of engine families covered by a waiver application if they used a catalyst replacement during the vehicles' useful life. My determinations were not influenced by the results of that examination, however, because I concluded that a required catalyst change does not constitute effective control technology for controlling CO emissions below the established standard. (See the discussion in Section III(B)(1)(a) of this decision).

I am applying the same conclusion regarding catalyst replacement in this consolidated decision as well. As a result, Appendix A to this decision does not project the emission capabilities of the engine families in question were they to employ such technology.

[34] Other factors (specifically, deletion of power enrichment and use of insulated or dual-walled exhaust pipes) representing CO emission control technology were considered available, but sufficient data to qualify these factors was not generally available therefore precluding their general use and thereby adding to the conservative nature of the analysis.

[35] The factors which the methodology employs to account for the effects of the respective improvements to emission control systems often is purposely low compared to measured effects of those factors on emissions.

[36] See, e.g., 40 FR 11900, 11908 (March 14, 1975), 38 FR 10317, 10323 (April 26, 1973). This is not the same methodology which the Administrator used in his initial decision, ultimately remanded by the Federal appellate court in *International Harvester Co. v. Ruckelshaus*, on applications for suspension of the 1975 model year HC and CO statutory standards.

[37] Certification testing is conducted under section 206(a)(1) of the Act on vehicle prototypes to determine whether those prototypes (incorporating the same designs as those intended for use in mass-produced vehicles) are capable of meeting Federal emission requirements. One part of the certification testing procedure involves conducting periodic emission tests on a representative "durability vehicle" while that vehicle accumulates 50,000 miles to see whether the vehicle exceeds Federal emission standards during that span. If an engine family passes certification testing, EPA issues a certificate of conformity permitting a manufacturer to introduce that family into commerce without violating section 203(a)(1) of the Act.

[38] These are the statutory standards which the Act has scheduled to take effect (absent a statutory waiver) in the 1981 model year. For the sake of simplicity, in discussing an engine family's projected ability to certify, I will refer to this set of standards by merely citing the 3.4 gpm CO standard.

[39] 43 FR 47272, 47276 (October 13, 1978). No applicants commented on the use of this methodology during the waiver proceedings. This methodology was the subject of considerable public comment before the Administrator first employed it to assess available technology as part of the remanded proceedings for suspension of the 1975 model year HC and CO standards. 38 FR 10317, 10323 (April 26, 1973).

[40] The Monte Carlo technique simulates 100 durability tests on a vehicle with available test data by statistically selecting for each simulated test a set of values for car-to-car, test-to-test, and deterioration rate variabilities over the range of values that could be expected to occur in conjunction with vehicles of the design in question. General Motors used this technique in analyzing emission test data as part of its submission for the proceedings for suspension of the 1975 model year HC and CO standards. See 38 FR 10317, 10323 (April 26, 1973).

[41] As explained in the first CO waiver consolidated decision, the Administrator also applied this 80% confidence level in the methodology he used in making his final decision on applications to suspend the 1975 model year HC and CO standards. In re: Applications for Waiver of Effective Date of the 1981 Model Year Carbon Monoxide Emission Standard for Light-Duty Vehicles, Consolidated Decision of the Administrator, 44 FR 53376, 53380, n. 47 (September 13, 1979). As Appendix B of the decision on the 1975 HC and CO standards explains, EPA has certified many engine families which had not passed certification testing requirements until the second attempt. Because the certification regulations permit an engine family more than one attempt at certifying, the statistical chances of that engine family passing certification testing (by passing on one of the two attempts) for a given pollutant actually are higher than 80%. In re: Applications for Suspension of 1975 Motor Vehicle Exhaust Emission Standards, Decision of the Administrator (April, 1973) (Appendix B).

account the test-to-test, car-to-car, and deterioration factor variabilities which cause uncertainty in projecting from the few test results provided by an applicant whether an engine family is likely to meet certification requirements when tested. This methodology therefore increases the reliability of projecting from available test results that an engine family will be able to meet certification requirements.

This results from this analysis indicate with high statistical confidence that most of the engine families which were covered by a waiver application and for which adequate emission test data were available can certify to the 3.4 gpm CO standard for the 1981 and 1982 model years. Appendix A provides an assessment for each engine family scenario and describes the adjustment factors employed in projecting each family's ability to certify.

B. Waiver Applications Granted

1. *Availability of Technology, Considering Costs, Driveability, and Fuel Economy.* a. *Unavailable Technology.*—I have determined that effective CO control technology, independent of considerations of costs, driveability, or fuel economy, is not available for 1981 model year vehicles of the Toyo Kogyo 91 and 120 CID engine families. These are the engine families which the Appendix A analysis projects as being unable to certify to the 3.4 gpm CO standard in 1981, even after incorporating any reasonably available adjustment factors based on available data (short of catalyst replacement) into the possible system designs as described by the waiver applicants.

I have determined generally that *effective* control technology is not available for engine families for the 1981 model year if those families could meet the 3.4 gpm CO standard only by employing a catalyst replacement during their useful life. Any technology requiring catalyst replacement is unlikely to be effective in controlling emissions to meet the 3.4 gpm CO standard because it requires consumers to assume a substantial extra burden in ensuring that engine families employing that technology continue to meet the CO standard. Specifically, this technology could require the consumer to assume additional costs (viz., the cost of the replacement) and/or additional inconvenience (leaving a car for repairs) which there is a natural inclination to avoid.

These disincentives would discourage consumers from obtaining the catalyst replacement while the vehicles are in use.[42] This effect would make it much less likely that, after the time scheduled for the catalyst replacement, these in-use vehicles of the engine families in question would continue to conform to emission standards. It is the Agency's continuing policy to encourage manufacturers to produce vehicles which will meet emission requirements effectively during their useful life. Denying a waiver application on the ground that a catalyst change can be part of an effective emission control system (without assurance that consumers will replace the catalyst in use) would encourage waiver applicants and other manufacturers to view catalyst replacement as an option in planning to produce automobiles to meet Federal emissions standards. Thus, I have not even considered catalyst replacement as a technological alternative in determing that effective control technology is not available for the two Toyo Kogyo families to meet the 3.4 gpm CO standard in the 1981 model year.

At the public hearing on its waiver applications, however, Toyo Kogyo indicated that additional emission control technology would be available for incorporation into 1982 model year vehicles of these two engine families. The Appendix A analysis projects that the two Toyo Kogyo engine families will be able to certify using that additional technology when it becomes available. As a result, the waivers which I have granted do not apply to 1982 model year vehicles of Toyo Kogyo's 90 and 120 CID engine families.[43]

b. *Costs, Driveability, and Fuel Economy.*—The Clean Air Amendments of 1977 added to the section 202(b)(5)(C)(iii) criterion the requirement to consider costs, driveability and fuel economy in assessing the availability of technology to meet the 3.4 gpm CO standard. Thus, an applicant can demonstrate that technology is not available by establishing that the costs (or driveability or fuel economy penalties) necessarily associated with progressing from the 7.0 gpm standard effective in model year 1980 to the 3.4 gpm goal set for 1981 are significant enough to make an engine family unable to remain reasonably competitive in the marketplace because that family would be unacceptable as an alternative for motor vehicle purchasers. For the two engine families receiving a waiver, it is unnecessary to consider costs, driveability, or fuel economy in determining the availability of technology for model year 1981, since I have already determined that effective control technology is not available for those families in the 1981 model year independent of those additional concerns.

c. *National Academy of Sciences Studies and Investigations and Other Information.*—As part of my assessment of technology, section 202(b)(5)(C)(iv) of the Act requires that I consider the results of NAS studies and investigations conducted under section 202(c) of the Act regarding available technology, processes, or other alternatives. In 1974, NAS published its most recent study under section 202(c) on technology available to meet the 3.4 gpm CO standard.[44] The 1974 study concluded that the technology was generally available to manufacturers to meet the 3.4 gpm standard, but only at the expense of a fuel economy penalty that would set the industry back to those levels the industry had been attaining in 1970.

Changes in the industry since 1974 limit the current value of this NAS study. Specifically, it is highly questionable whether the fuel economy concerns raised in 1974 still apply to the current state of technology. Since the 1974 report, Congress has passed the Energy Policy and Conservation Act (EPCA)[45] to ensure that the industry achieves specified levels of fuel economy performance. None of the current set of waiver applicants even claimed that it would face problems in meeting the Corporate Average Fuel Economy (CAFE) requirements.[46] Moreover, none of the applicants established that an unacceptable fuel economy penalty will result for an engine family in question if a waiver covering that engine family is not granted.[47] In light of these considerations, requiring attainment of the 3.4 gpm CO standard generally is unlikely to have a significant adverse effect on the fuel economy levels actually attained by waiver applicants in the 1981 model year.

The NAS has not produced any relevant studies or investigations since 1974. EPA has contracted for NAS to

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[42] Consumer response rates to emission related recalls indicate that even where replacement is free of charge, a substantial number of vehicles do not receive repairs.

[43] See the discussion of these two Toyo Kogyo engine families in Section III(C)(1)(a) of this consolidated decision.

[44] Report by the Committee on Motor Vehicle Emissions of the National Academy of Sciences, dated November, 1974.

[45] Pub. L. No. 94–163, 89 Stat. 871 (1975).

[46] See section VIII of Appendix A and the discussion in section III (C)(1)(b)(iii) of this decision. The so-called CAFE requirements are the manufacturers' sales-weighted fuel economy standards set under § 502 of EPCA.

[47] *Id.*

provide in the near future an updated version of its 1974 study on the feasibility of complying with a 3.4 gpm CO standard.

The available studies and investigations from NAS drew general conclusions about the availability of effective control technology to the light-duty vehicle industry on the whole rather than for specific engine families. The 1977 amendments to the Act, however, require that I assess the availability of technology for specific vehicle or engine models covered by a waiver application. Thus, the findings of the available NAS studies do not directly contradict my assessment regarding the unavailability of technology for the two Toyo Kogyo engine families for which I have decided to grant a waiver for the 1981 model year.

In addition, my review of available technology has encompassed other information incorporated into the record from nonapplicant manufacturers and from part suppliers and developers in response to subpoenas issued under section 307(a)(1) of the Clean Air Act. [48] Some non-applicant manufacturers have expressed concerns over their respective technological abilities to achieve the 3.4 gpm CO standard by the 1981 model year.[49] Many of the concerns they raised, however, only addressed the potential extra costs of the technology which those manufacturers projected to be necessary to achieve a 3.4 gpm standard and did not contest the availability of technology to meet that standard.[50]

In assessing the availability of technology, I also have reviewed data from emission tests performed on vehicles for the purpose of receiving certification for the 1980 model year. In making my determinations, I only considered test data obtained from vehicles whose emissions characteristics could be considered reasonably representative of the emissions performance of an engine family covered by a waiver application.

This additional information, as well as other information available to me and included in the record, does not provide an adequate basis for me to alter any conclusions I have reached so far in this decision regarding the unavailbility of technology for the Toyo Kogyo 91 and 120 CID engine families.

2. *Protection of the Public Health.*—Section 202(b)(5)(C) of the Act requires that before I grant a waiver covering a given engine family, I must find that protection of the public health does not require attainment of a 3.4 gpm CO standard by the vehicles of the engine family receiving the waiver for the model year to which the waiver applies. Thus, I have examined this issue with respect to the two Toyo Kogyo engine families for which I have determined that effective control technology, considering costs, is not available in model year 1981. I have found as a result of this examination that any health effects resulting from waiving the 3.4 standard for the 1981 model year for either or both of these two engine families would be insignificant. The same statement is true regarding the combined health effects resulting from waiving the 3.4 standard for the 1981 model year for these two Toyo Kogyo engine families and for all the 1981 and 1982 model year engine families receiving waivers under the first consolidated CO waiver decision. As a result, protection of the public health does not require the two Toyo Kogyo engine families, for which I have determined that effective CO control technology is not available, to attain a 3.4 gpm CO standard for the 1981 model year.

The appropriate starting point for determining whether ambient CO levels protect public health is the National Ambient Air Quality Standards (NAAQS) for CO, which have been established under section 109(a) of the Act by regulations of the Administrator.[51] The "primary" (i.e., health-protective) NAAQS for CO are 9.0 parts per million (ppm) ppm as measured over an eight-hour period and 35 parts per million (ppm) as measured over a one-hour period.[52]

Studies have demonstrated that most (and in some areas, almost all) ambient CO originates from motor vehicles.[53] In setting a statutory CO emission standard for light-duty motor vehicles as part of the 1970 amendments to the Act, Congress determined that a 90% reduction from emission levels permitted by the CO standard in effect in 1970 was necessary to permit nationwide attainment of the NAAQS for CO.

The record for the proceedings at hand does not contain any information precisely assessing on an engine family-by-engine family basis the effects on ambient CO levels of granting a two-year waiver of the effective date of the 3.4 gpm CO standard. Appendix B to this decision, however, reviews the informaton contained in the record and provides an evaluation of the effects of an industry-wide CO waiver.[54]

Appendix B uses EPA's rollback modeling technique [55] to project the effect which an industry-wide CO standards, waived to 7.0 gpm and in effect for 1981 and 1982 model year vehicles, would have during 1981–1985 on the following matters: the reductions in ambient CO concentrations [56] the number of areas from among the nation's 19 worst low-altitude, non-California air quality control regions (AQCRs) for CO that would exceed the health-based NAAQS for CO, and the number of violations occurring within

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[48] Much of this information was gathered for an included in the record for the first consolidated CO waiver decision. See EPA Public Docket EN-79-4. That record has been incorporated by reference into the record for this second consolidated decision. See EPA Public Docket EN-79-17. The latter record also contains information which was not received in time for consideration in the first consolidated decision.

[49] Ford Motor Company stated it still was uncertain whether its engine families would be able to certify to the 3.4 CO standard in 1981 (July 10 Tr., p. 204). See also, e.g., the testimony of Saab-Scania of America, Inc. (July 11 Tr., p. 5).

[50] See, e.g., the testimony of Ford (July 10 Tr., p. 209) or AB Volvo (July 11 Tr., p. 92). AB Volvo explicitly stated its belief that technology is available to enable its engine families to meet the statutory 1981 standards at additional costs (July 12 Tr., p. 94).

[51] 40 CFR 50.8 (1978).

[52] These standards were established by correlating ambient CO levels with observed negative health effects and factoring in a margin of safety. I am not undertaking a review of these standards as part of thee proceedings.

[53] See, e.g., Joint Comments from Environment Defense Fund and National Resources Defense Council, p. 9 (July 30, 1979); T. App., p. 2–15.

[54] Appendix B addresses the significant comments which waiver applicants in either the first or second set of waiver proceedings have submitted to the record regarding the projected effects of CO waivers on ambient air quality and the public health. The waiver applications under consideration in this consolidated decision for the most part state merely that the respective applicant's projected share of total 1981 and 1982 model year vehicles sales will be so small as to render the contributions of the applicants' vehicles to ambient CO levels insignificant.

Nissan was the only applicant to raise additional matters in this area. N. App. 2.1–2.3. The substance of each of these comments already had been entered into the record by other parties submitting information for consideration in the first consolidated decision, and those comments were addressed in Appendix B to that decision. As a result, Appendix B to this decision is virtually the same as Appendix B of the first consolidated decision.

[55] The rollback model basically assumes a proportional relationship in calculating CO concentration in the atmosphere on the basis of the rate of CO emissions. A mathematical description of the rollback model is presented in an EPA memorandum from Edward J. Lillis to Charles L. Gray, dated May 14, 1979, and included in the record for these proceedings.

[56] As described by the highest second highest CO reading from any of the 19 air quality control regions examined. The analysis examines the second highest CO reading in a region to represent the maximum ambient CO level reached during a given year so as to negate any biasing effect which an extraordinarily high measurement due to highly unusual meteorological conditions might cause.

these 19 areas under each of several possible sets of variable conditions (such as the rate of in-use deterioration or the type of emission control system incorporated into vehicles in use).

The extent to which each of these developments occurs naturally depends upon the set of conditions assumed by the projections to be in effect and therefore differs to some extent from several of the projections included in the record. In a "maximum difference" or "worst case" scenario, Appendix B projects that in 1985, for example, an industry-wide waiver could cause a 4% decrease in the reduction of ambient CO concentrations. Under those circumstances, the industry-wide waiver would cause a 33% increase in the number of CO NAAQS violations which could occur in these AQCRs and an increase from 11 to 12 in the number of "non-attainment" regions [57] in this group.

In Appendix B's projections under a scenario employing a set of "nominal" or "reasonable" conditions judged more likely to occur, however, the effects of an industry-wide waiver would be less pronounced. Under these circumstances, Appendix B projects no measureable change in 1985 ambient CO concentrations, no change in the number of nonattainment regions, and only a 5% increase in the total number of CO NAAQS violations.

In light of these projections for a two-year, industry-wide waiver, the incremental contribution to ambient CO levels from an individual engine family receiving a waiver would constitute such a small portion of these effects on ambient CO levels that I find it reasonable to characterize that contribution as insignificant. The information supplied to the record by waiver applicants in these proceedings and in the proceedings associated with the first consolidated CO waiver decision supports this conclusion regarding the incremental contributions of individual engine families.

I also have found that the sum of the incremental contributions to ambient CO levels from the two Toyo Kogyo engine families for which I have determined under this decision that effective control technology, considering costs, driveability, and fuel economy is not available for the 1981 model year still is so small even when combined with the incremental contributions from those engine families receiving waivers under the first consolidated CO waiver decision, as to be insignificant in its effect on public health.[58] This combined projected effect should still be small enough to avoid the need for any modification of any State Implementation Plan (SIP) adopted according to the requirements of section 110 of the Act for the purpose of attaining the NAAQS for CO.

3. *Essential to the Public Interest or to the Public Health and Welfare.*—Before I may grant a waiver request, section 202(b)(5)(C)(i) of the Act requires that I determine that granting the waiver is essential to the public interest or the public health and welfare. I have determined that it is essential to the public interest to grant the waiver requests covering the two Toyo Koygo engine families for which I have determined that effective CO control technology is not available.

I have based this determination on the need to protect the public's interest in preserving diversity and competition in the automobile industry. Denying a waiver for either of the 1981 model year Toyo Kogyo engine families which lacks the technology to continue in production under the 3.4 gpm CO standard would reduce the diversity of choices available to consumers to that extent.[59] Denying these waivers also could create a threat to Toyo Kogyo's overall ability to continue as a competitive force in the marketplace and therefore to the viability of that applicant as a manufacturer of automobiles. If Toyo Kogyo could not remain viable as a manufacturer, Toyo Kogyo would no longer market other engine families which would be capable of meeting applicable emission requirements; thus, diversity and competition in the automobile industry would be undermined even further.

This problem assumes added import in an instance in which a relatively small-volume manufacturer such as Toyo Kogyo is concerned. Thus, if I denied the waiver applications covering the two Toyo Kogyo engine families for which I have determined effective CO control technology is not available, I would be creating a high degree of risk that the range of choices available to meet the automotive needs of consumers may decrease. This result could only interfere with the effectiveness with which the automobile industry is able to meet market demand for automobiles and therefore is potentially detrimental to the public interest.[60]

In this case, in which I already have determined that granting waivers for Toyo Kogyo's two 1981 model year engine families for which effective control technology is not available would not measurably impair public health, I have concluded that it also is essential to the public interest to allow Toyo Kogyo to produce these engine families by granting the waiver applications covering these 1981 model year engine families.

4. *Good Faith.*—In order for me to grant a waiver to any applicant, section 202(b)(5)(C)(ii) of the Act requires that I determine that the applicant in question has made all good faith efforts to meet the emission standards established by this subsection. In the context of this consolidated decision, therefore, I have examined information regarding each applicant's previous and projected efforts toward meeting a 3.4 gpm CO emission standard for the engine families in question.

In response to the waiver application guidelines and Agency subpoenas, each applicant has submitted detailed, specific descriptions of its past, present, and future programs for development of CO emission controls. As a basis for comparisons, the record contains similar submissions from earlier waiver applicants and other automobile manufacturers which have not filed waiver applications.

To the extent that information contained in the record relates to the good faith criterion, it tends to support a finding confirming the good faith efforts of each applicant at developing CO emission controls. In some instances, however, the applicant's showing in this regard is at best marginal.[61] The

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[57] An AQCR is a "non-attainment" region if measurements in that region produce results which exceed either one of the NAAQS for CO more than one per year.

[58] The engine families receiving waivers under both the first and second consolidated CO waiver decisions only constitute approximately 12% of total projected 1981 model year light-duty vehicle sales in the United States.

[59] This problem was raised by waiver applicants during the proceedings associated with the first consolidated CO waiver decision. See AMC App., p. 3; C. App. Vol. I, p. III-2.

[60] For example, Ford, a non-applicant, indicated in its testimony during the public hearing for the first consolidated CO waiver decision that as a competitor it would have problems meeting the extra market demand created when an applicant would be unable to market an engine family which could not meet a 3.4 gpm CO standard. Specifically, Ford explained that, because it would receive notice of that extra market demand only shortly before the 1981 model year, it would not have sufficient lead time to meet any more of that demand than already-existing idle capacity would permit. July 10 Tr., p. 203.

[61] An area that especially concerns me is the paucity of data from the applicants (including Toyo Kogyo) on systems that would appear to represent best effort technology. Another area of equal concern to me centers on the Nissan engine families for which I could not make a pass/fail determination due to the lack of sufficient data submitted by the applicant on any systems. Therefore, I have to deny the waiver applications covering these vehicles. This "no data" category encompasses two "no data" families out of a total of six (or 33%) planned by Nissan for the 1981 and

Footnotes continued on next page

applicant's financial information is general and therefore difficult to evaluate in the context of this decision. Nevertheless, I have no basis for concluding that any significant discrepancy exists among themselves or among manufacturers generally with respect to the amounts of resources, relative to company size, which each applicant has committed to the development of CO emission controls.

Of course, each applicant has a natural motivation to present its good faith arguments in the best light possible. The record contains little, if any, evidence from disinterested sources which directly corroborates the information supplied by the applicant.

In *International Harvester Co. v. Ruckelshaus,*[62] the court discussed the relative burdens and standards of proof present in proceedings such as these. The court stated that once an applicant produces ostensibly reliable and specific information in support of its position, the Administrator bears the burden of showing the reliability of any methodology employed in reaching a decision adverse to the evidence presented by the applicant. In this case, I have concluded that I could not reasonably reach a determination that any of the applicants in these proceedings has not taken all good faith efforts to meet the 3.4 gpm CO emission standard. Information submitted by an applicant might tend to ignore or gloss over information pertaining to an existing or potential CO control technology which the applicant failed to pursue in good faith. Nevertheless, the record contains no information indicating that a given applicant acted in bad faith, and therefore provides no basis for refuting the information supplied by the applicants.

Thus, I have determined that each applicant (including Toyo Kogyo) has demonstrated compliance with the good faith criterion set forth in section 202(b)(5)(c)(iii) of the Act.

5. *Conclusion.*—Both of the Toyo Kogyo engine families for which I have determined that effective CO control technology is not available for the 1981 model year are covered by waiver applications which meet each of the remaining criteria under section 202(b)(5)(C) of the Act. As a result, I am granting a waiver of the effective date of the 1981 statutory CO emission standard for both of these engine families for the 1981 model year.[63]

C. *Waiver Applications Denied*

1. *Availability of Technology, Considering Costs, Driveability and Fuel Economy.* a. *Available Technology.*—Appendix A projects the following engine family to be capable of passing certification testing requirements if that family uses one of the applicant's specified emission control system designs which the applicant is considering for possible use to meet the 3.4 gpm CO standard:

Manufacturer	Engine family
Nissan	119 CID

Nissan provided emission test data from a vehicle (VIN YD021) using its 119 CID engine with a fast burn/fuel injection/exhaust gas recirculation/three-way catalyst system. Appendix A's Monte Carlo analysis indicated with a high degree of confidence that this engine family could pass certification testing.

In addition, Appendix A projects that the following remaining engine families including Nissan's 119 CID engine family are capable of passing certification testing:

Manufacturer	Engine family	Adjustment factors [64]
Nissan	85/91 CID [65]	Ignition timing recalibration during cold start.
	119 CID [66]	Improved oxidation catalyst and dual-walled exhaust pipe.
	146/168 CID	Warm-up air injection.
Toyo Kogyo	91 CID (1982 model year only).	Clean-up oxidation catalyst with switched-air system.
	120 CID (1982 model year only).	Clean-up oxidation catalyst with switched-air system.

Based on evidence submitted by Toyo Kogyo, I have determined that effective CO control technology (specifically, a system Toyo Kogyo has been developing which uses a feedback carburetor and oxygen sensor) which is not available for Toyo Kogyo's 1981 model year vehicles will be available for the 1982 model year.[67] Otherwise, I have determined on the basis of the projections in Appendix A that effective CO control is available as of the 1981 model year to the engine families in the two preceding lists.

I also have decided that, for the following engine families, the respective applicants have failed to establish that effective control technology is not available to enable these engine families to meet the 3.4 gpm CO standard:

Manufacturer	Engine family	Adjustment factor
Fuji	97 CID	Either: (a) Improved three-way catalyst and a clean-up oxidation catalyst with an aspirator between the catalysts or (b) improved three-way catalyst and a clean-up oxidation catalyst with a switched-air system.
	109 CID	Either: (a) Clean-up oxidation catalyst with aspirator between catalysts or (b) clean-up oxidation catalyst with switched-air system.
Renault	85 CID	Clean-up oxidation catalyst with switched-air system.
Nissan	75 CID	None used.
Toyo Kogyo	70 CID (Rotary)	None used.

Footnotes continued from last page

1982 model years. This lack of demonstrated effort with respect to these engine families touches on the good faith issue directly. I have denied these "no data" applications, but the 1981 model year certification process is already underway. It would appear that the 1981 certification process will be the first time Nissan conducts sufficient durability testing on these "no data" engine families to determine if they can certify at the 0.41 HC, 3.4 CO, 1.0 NOx standards.

Although I cannot refuse an application for certification on the basis of the absence of what I consider to be best effort technology, I am again putting the industry on notice that applications for waiver of the 3.4 CO standard, based on 1981 certification data generated by less than best effort technology, will be evaluated very carefully in light of the "all good faith efforts" criterion of the statute. I already have referred to this problem with respect to applications considered for the first consolidated CO waiver decision. See 44 FR 53383, n. 67 (September 13, 1979).

[62] 478 F.2d 615 (D.C. Cir. 1973).

[63] Given the conservative nature of the analysis used to project that effective control technology is not available for these engine families, it remains possible that some of these families still might be able to meet the 3.4 gpm CO standard. Even with my decision to grant waivers for these families, I still expect the applicants to make reasonable attempts to have these families meet the 3.4 gpm CO standard.

[64] Section IV of Appendix A explains how these factors were developed and applied.

[65] Indeed, a durability vehicle which did not employ any improvements from this engine family already has produced emission test results during 1980 California certification testing which meet the 1981 Federal emission standards. These data tend to confirm the projection of the Monte Carlo Analysis regarding this emgine family's ability to meet the 3.4 gpm CO standard.

[66] As noted earlier in this section, Appendix A's analysis indicated that one of the emission control systems which Nissan had tested for this engine family is capable of meeting the 3.4 gpm CO standard in 1981. The analysis also demonstrated that another emission control system (fast burn/pulse-air injection/exhaust gas recirculation/oxidation catalyst) which Nissan tested for this engine family could meet the 3.4 gpm CO standard by using the adjustment factors as specified. The dual-walled exhaust pipe factor was derived from data supplied by Nissan (see discussion in Appendix A) and was applied for the 119 CID family because Nissan indicated that feature would be available by the 1981 model year.

[67] See Section III of Toyo Kogyo's letter (undated) to Marvin B. Durning, EPA's Assistant Administrator for Enforcement, responding to questions raised at the public hearing on September 12, 1979. See also Sept. 12 Tr., pp. 42–44.

Both Fuji and Renault claimed that space limitations prevented them from incorporating needed emission control components into vehicles of their 97, 109, and 85 CID engine families to enable those engine families to meet the 3.4 gpm CO standard. Fuji stated that it could not fit either a heat shield for an oxidation catalyst or an air pump for a switched-air injection system into its vehicle designs.[68] Renault asserted that because of space constraints it could not locate a clean-up oxidation catalyst close enough to the engine to improve efficiency.[69] Appendix A projects that these engine families could not meet the 3.4 gpm CO standard unless they incorporate these specified design features.

The illustrations and photographs which these two applicants have submitted to the record to substantiate their respective space constraint claims have not been sufficient to establish the physical impracticability of including the necessary additional equipment or design modifications. As a result, I have determined that Fuji and Renault have failed to establish that effective control technology is not available to enable these engine families to meet the 3.4 gpm CO standard. If these two applicants fail in their attempts to incorporate physically the technology capable of meeting the 3.4 gpm CO standard, they can reapply for waivers covering these engine families on the basis of more conclusive information regarding their respective inabilities to incorporate the necessary improvements into their vehicle designs.

The Monte Carlo analysis projected with a high degree of confidence that Nissan's 75 CID engine family without adjustment factors [70] would be able to certify to the 1981 statutory emission standards for HC and CO. The level of confidence with which the Monte Carlo analysis predicted this engine family could certify to the 1981 NO_x standard fell slightly below the level required for me to conclude under this decision's conservative approach that effective control technology is available to achieve compliance with that standard.[71]

However, Nissan submitted emission data from 1980 California certification testing on a durability vehicle of this engine family which met all three 1981 Federal emission standards for 50,000 miles.

The Monte Carlo analysis only predicts how an engine family is likely to perform in certification testing, whereas the California results constitute actual certification performance.[72] This decision normally employs a highly conservative approach in order to minimize the risk of incorrectly projecting that the necessary technology is available to an applicant. In this case, the California certification data provide me with an independent basis for concluding that the risk of incorrectly determining that the applicant has failed to establish the unavailability of technology is properly minimized for the Nissan engine family as well.[73] Nissan actually is producing 1980 model year California vehicles of the 75 CID engine family subject to emission standards for NO_x and HC equal to the 1981 Federal standards for those pollutants. In this case, it so happens that at 50,000 miles Nissan's certification vehicle also met Nissan's emission design target for a 3.4 gpm CO standard. Thus, even according to Nissan's own criteria it appears highly probable that this engine family is capable of meeting 1981 Federal emission standards. Based on this information, I cannot conclude that Nissan has established, as section 202(b)(5)(C)(iii) of the Act requires, that technology is not available to enable this engine family to meet 1981 Federal emission standards.

Appendix A's analysis of the engine families covered by Toyo Kogyo's waiver application indicated that Toyo Kogyo's 70 CID (rotary) engine with open-loop carburetor/multi-catalyst systems would not be capable of meeting the 3.4 gpm CO standard in the 1981 model year. However, Toyo Kogyo also submitted emission results from 1980 California certification testing on a vehicle using this engine with an exhaust gas recirculation/air injection/thermal reactor emission control system without a catalyst. The results from this durability testing were below 1981 Federal emission standards for all regulated pollutants.

Appendix A could not include a Monte Carlo analysis of Toyo Kogyo's thermal reactor system on the 70 CID engine. This is the case because the test-to-test, car-to-car, and deterioration variability factors which the Monte Carlo simulation applies are based on data generated by vehicles employing catalyst technology; hence, these factors most likely are not representative of the variabilities likely to occur for engine families not employing catalysts. Sufficient information is not otherwise available to me to develop these variability factors for this system.

Because the Monte Carlo analysis cannot be applied to Toyo Kogyo's 70 CID engine using the thermal reactor system, the California certification data is the only information in the record which is directly indicative of the emissions performance capabilities of this engine family. Because these California certification test results meet the 1981 Federal emission standards, I cannot conclude that Toyo Kogyo has established that effective control technology is not available to enable this engine family to meet the 3.4 gpm CO standard in the 1981 model year. As was the case with the Nissan 75 CID engine family, I have concluded on the basis of available California certification data that the risk of incorrectly determining that Toyo Kogyo has failed to establish the unavailability of technology for its 70 CID engine family also is properly minimized.[74]

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[68] Sept. 12 Tr., pp. 117–121, 128.

[69] R. App., p. V/4.

[70] No data were available to permit adjustment factors to be properly applied to this family for the Monte Carlo analysis.

[71] The Monte Carlo simulation resulted in a 77% probability that this engine family could meet the NO_x standard. This decision has used an 80% confidence level as the cutoff point for concluding that effective control technology is available.

[72] The durability test results obtained for this engine family in 1980 California certification can be used to satisfy the durability test requirements for 1981 Federal certification.

[73] Data from 1980 California certification which indicate the capability of a vehicle to meet the 1981 Federal emission standards may be useful in evaluating the technological capabilities to meet the 1981 federal standards. However, this is not to suggest that in every instance where an engine family has certified to California's 1980 standards at levels that indicate it could also meet 1981 federal standards, that I must conclude the manufacturer has failed to establish that the technology is not available to meet those federal standards. A manufacturer may be able to establish that California certification data for one reason or another are not representative of the engine family's true capability to meet the 1981 federal standard. (See e.g. Chryslers 3.7L family at 44 FR 53394). In such situations, the California certification data alone are not determinative as to the availability of technology.

[74] Toyo Kogyo can use the 1980 California durability certification results to meet the 1981 Federal durability certification requirements associated with a 3.4 gpm CO standard. While this may not represent Toyo Kogyo's sole criterion for determining whether to produce this engine family, these certification results essentially provide Toyo Kogyo with a license to produce this family (presuming that this family will be able to pass the remaining 1981 Federal certification testing requirements apart from the durability testing requirements). Reducing the risk that families which don't meet emission requirements will go into production is a principle objective of the certification program. However, a manufacturer may elect not to accept the certification results and not to produce such a "certified" family based on its independent assessment of the risk of noncompliance with emission standards in actual use. Toyo Kogyo has stated that it has not and would not produce an engine family that did not meet its design targets, presumably as a statement of how it addresses this risk; nevertheless Toyo Kogyo has certified and produced this family for California under HC and NO_x standards that are identical to 1981 federal standards, even though that

Footnotes continued on next page

Each of the applicants has argued that inquiry into whether a waiver applicant has met the technology-related criteria established by the Act for receiving a waiver does not end with the evaluation of whether an engine family is capable of certifying to the 3.4 gpm standard. The applicants assert that proper consideration of this area also should take into account the prospects for an engine family's complying with the other emission-related statutory requirements should be the 3.4 gpm CO standard go into effect.

More specifically, the applicants contend that factors such as prototype-to-production slippage, production variation, and in-use deterioration create a significant risk that production vehicles will not meet the applicable CO emission standard either coming off the assembly line or in use.[75] Under those circumstances, the manufacturer could be subject to liability under EPA's assemblyline testing, recall, and warranty programs. For this reason, the applicants have developed their own emission design targets below the actual CO standard. The applicants contend that only after they meet these targets have they assured themselves that they have minimized to an acceptable level the risk of mass producing vehicles exceeding the CO standard.

I have determined that none of the waiver applicants has established that technology will not be available to enable the engine families which I cannot conclude are incapable of passing certification requirements also to be capable of meeting the 3.4 gpm CO standard during their useful life after those families go into mass production.

Section 202(b)(5)(C)(iii) of the Act clearly places the burden of making the necessary showing regarding the available technology criterion with the applicant. EPA specifically indicated the significance of this explanation by requesting information on this point in its "Guidelines for Applications for Waiver of the 1981 Carbon Monoxide Emission Standard" (43 FR 47272, 47276 (October 13, 1978)), in the subpoenas it issued to the waiver applicants, and in the questions propounded to the applicants during the public hearing.

The applicants here for the most part have provided EPA with their design targets and with an explanation of the factors considered in deriving the design targets for the respective engine families.[76] However, no applicant has had any production experience under a 3.4 gpm CO standard through which it could establish relevant prototype-to-production slippage rates or ranges of variations among production vehicles. The availability of this information would have improved the accuracy of any projections as to whether an engine family capable of passing certification testing also could meet Federal emission requirements in mass production.

As explained in the discussion on decision methodology in section III(A)(2) of this decision, the projections of available technology in Appendix A are intentionally conservative in an effort to factor in considerations pertaining to any possible risks that engine families will not meet standards when they are mass produced. Appendix A's Monte Carlo simulation methodology accounts for the variation in deterioration rate that may occur between vehicles in projecting the ability of those tested vehicles in question to meet the 3.4 gpm CO standard for 50,000 miles (the vehicles' statutory useful life according to section 202(d)(1) of the Act). The methodology also statistically applies test-to-test and vehicle-to-vehicle variation factors, and thereby accounts for much of the effects of those variations in production. Thus, I am unable to conclude that any applicant has established that possible differences in an engine family's emission control capabilities between certification and production create an unacceptable risk that available technology capable of meeting a 3.4 gpm CO standard during certification testing will not meet the 3.4 gpm CO standard once that technology is introduced into mass production.[77]

The record did not include sufficient information to make any conclusive determination regarding available technology for the following engine families:

Manufacturer	Engine family
Nissan	EF-A EF-B

The waiver applications covering these engine families included no emission test results which the decision's prescribed methodology could use as a basis for evaluating their respective CO emission control capabilities, even though the waiver application guidelines expressly specified the form for the test data.[78] Moreover, no engine families for which Nissan did submit sufficient test data were similar enough to these "no data" engine families to provide a basis for assessing the capabilities of those engine families.

As I have mentioned earlier in this section, the Act places with the applicant the burden of establishing the lack of available technology. By failing to supply sufficient data from any engine family through which I can assess adequately the CO emission control capabilities of that particular engine family, the applications I have received covering Nissan these engine families have failed to meet the burden which the Act imposes on them. Thus, I cannot determine that, independent of considerations of costs, driveability, and fuel economy, effective control technology is not available to these two Nissam engine families.

Footnotes continued from last page

family did not meet its stated design targets in certification for these pollutants. Toyo Kogyo has provided no additional data to further my ability to assess the risks associated with production of this family. Therefore, I have no reason to believe that Toyo Kogyo faces an unreasonable risk in marketing this family on a national basis as well. This is contrasted with the situation involving Chrysler's 3.7L engine family (44 FR 53394).

[75] See, e.g., Fuji App., pp. 1-3; N. App., 1.7.

[76] Fuji App., pp. A-2-1 to A-2-3; Fuji. 9/18/79, pp. S-8-1 to S-8-2. N. App., pp. 5.4.1 to 5.4.2 and Attachment V. R. 9/24/79, pp. 4.1 to 4.4. Section V of Toyo Kogyo's letter (undated) to Marvin B. Durning, EPA's Assistant Administrator for Enforcement, responding to questions raised at the public hearing on September 12, 1979.

[77] The Nissan 75 CID and Toyo Kogyo 70 CID engine families have not passed the conservative Monte Carlo analysis (the latter because data were not available to permit proper application of the Monte Carlo simulation to that family). Nevertheless, I cannot conclude that these applicants have established that effective control technology is not available to these families. An applicant for waiver of emission standards has a natural incentive to provide conservative design targets to project the emission performance of its vehicles in production. Since neither Nissan nor Toyo Kogyo established how failure to meet their respective design targets would cause them to be incapable of meeting emission requirements for production and in-use vehicles, it is inappropriate for me to view not meeting such targets as requiring determination that technology is unavailable. Further, these manufacturers failed to relate the design targets to their actual behavior in the market place, since both have marketed vehicles in California under emission standards for those pollutants where those vehicles failed in certification testing to meet their respective targets associated with those standards.

[78] See "Guidelines for Application for Waiver of the 1981 Carbon Monoxide Emission Standard," 43 FR 47272, 47276 (October 13, 1978). In order to be adequate for use in the analysis, the emission test data must come from a vehicle which has accumulated at least 20,000 miles with no major emission control component or calibration changes and has been subject to at least four valid tests according to the 1975 Federal Test Procedure. Generally speaking, the data which Nissan submitted for the engine families in question here did not come from vehicles which had accumulated the mileage necessary to give some indication of the vehicles' durability characteristics.

In contrast, I am able to reasonably base a decision regarding the availability of technology on the emission test results for Toyo Kogyo's 70 CID engine family using a thermal reactor, even though they were not capable of analysis by the Monte Carlo simulation. Those data at least gave some indication of the engine family's durability because its emissions were measured periodically over the course of the test vehicle accumulating 50,000 miles.

Section V of Appendix A contains a more complete discussion of how the methodology applied the emission information which manufacturers submitted.

Nissan may reapply for waivers for these "no data" engine families. At that time, I will re-examine the availability of effective control technology for those engine families in light of any new, sufficient emission test data which Nissan may provide.

b. *Costs, Driveability, and Fuel Economy.*—I also cannot determine for each of the engine families not granted a waiver that, even after considering costs, driveability, and fuel economy, effective control technology is not available to enable these engine families to meet a 3.4 gpm CO standard in the 1981 model year. Specifically, neither the separate nor the combined effects of the costs, driveability, and fuel economy considerations associated with meeting a 3.4 gpm rather than a 7.0 gpm CO standard are significant enough to make any of these engine families unable to remain reasonably competitive in the marketplace.

i. *Cost.*—Appendix A analyzes the costs on a manufacturer-by-manufacturer basis of meeting the statutory CO standard based on 1979 dollars. Table VI-2 in Appendix A provides the following list detailing the extra costs per vehicle (for those families not receiving a waiver) which EPA projects that a manufacturer would have to incur in marketing each engine family covered by a waiver application with systems targeted at a 3.4 rather than a 7.0 gpm CO standard:

Manufacturer	CID	Extra cost (1979 dollars)	
		1981	1982
Fuji	97	$91-$128	$91-$128
		$95-$137	$95-$137
Nissan	75	$35	$35
	85/91	$0	$0
	119	$12	$12
Renault	146/168	$48	$48
		no data	no data
		no data	no data
Toyo Kogyo [79]	70	−$105	−$105
	91	$0 (fail)	$10
	120	$0 (fail)	$10

[79] Toyo Kogyo's projected cost difference for its 91 and 120 CID engine families between its designated first-choice emission control system and a system projected in Appendix A to be best capable of meeting the 3.4 gpm CO system differs between the 1981 and 1982 model years because of additional emission control equipment which will not be available for implementation into production until the 1982 model year. For its 70 CID family, Toyo Kogyo apparently prefers its first-choice system, even though it is more expensive than the system Appendix A finds most capable of meeting the 3.4 gpm CO standard as quickly as possible because its first-choice system achieves greater fuel economy gains.

The manufacturers' own estimates of their respective cost differences in attempting to meet the 3.4 versus the 7.0 gpm CO standard are listed in Appendix A's Table VI-3 as follows:

Manufacturer	Extra cost (1979 dollars) (Sales-weighted averages)
Fuji	$80-$100
Nissan	$57-$104
Renault	Confidential
Toyo Kogyo	$50

These added costs are not large enough to affect significantly the competitive position of any of the engine families not receiving waivers.[80]

ii. *Driveability.*—I also have determined that the sacrifices in vehicle driveability associated with implementing the technology necessary to meet the 3.4 gpm CO standard would not make any of the engine families in question an unacceptable alternative to consumers. For the most part, the applicants included only general allusions to driveability concerns in stating their respective cases for waivers.[81] Thus, I have no adequate basis for concluding that driveability concerns prevent effective control technology from being implemented on any engine family covered by a waiver application.

iii. *Fuel Economy.*—I also have determined that any fuel economy penalties associated with effective CO control technology would not seriously impact the acceptability to consumers of the engine families in question. Indeed, at least some applicants confirmed that technology designed to meet the 3.4 gpm standard in model year 1981 incorporated features which actually improve fuel economy relative to meet the current less stringent CO standard for 1979 model year vehicles.[82]

No applicant contended that the failure to receive a waiver would preclude the applicant from achieving the Corporate Average Fuel Economy (CAFE) requirements imposed by the Energy Policy and Conservation Act. Toyo Kogyo was the only applicant which projected a specific fuel economy penalty (estimated at 5% for its "first-choice" systems for both its rotary and conventional engines) associated with meeting a 3.4 gpm CO standard relative to levels it would be capable of attaining in conjunction with its suggested 7.0 gpm interim standard for 1981 model year vehicles.[83] Nissan was the only other applicant to suggest a specific figure for the fuel economy penalty it expected to incur (projecting a net loss of from one to two percent).[84] This information does not establish that the fuel economy penalties are significant enough to prevent associated technology from being incorporated into 1981 model year vehicles which would be acceptable to consumers and therefore still could be marketed competitively.

Thus, I have determined that considerations of costs, driveability, and fuel economy, whether evaluated separately or in combination, do not give me a basis for concluding that effective control technology is not available for the engine families which Appendix A either projects to be capable of attaining the 3.4 gpm standard or, for one of several reasons, cannot project to be incapable of attaining that standard. For that reason, I am denying the waiver applications under consideration insofar as they apply to these engine families.

c. *National Academy of Sciences Studies and Investigations and Other Information.*—As explained in section III(B)(1)(c) of this decision, the most recent study by the NAS (published in 1974) on the availability of technology to meet a 3.4 gpm CO standard concluded that the requisite technology (at the expense of a fuel economy penalty) was available to the industry as a whole, but reached no conclusions regarding the availability of technology on an engine family-by-engine family basis. As this earlier discussion also explained, the fuel economy penalty projected for technology available in 1974 is not a significant concern now.

Thus, I have determined that the results of the available NAS studies and

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[80] Of course, to the extent that each manufacturer incurs some extra costs in meeting the 3.4 gpm CO standard, the effect of the extra costs on the competitive positions of the engine families of each waiver applicant will be mitigated. The same is true regarding any extra driveability or fuel economy problems that an applicant may experience. See also the discussion of costs in section III(C)(3) in the public interest criterion.

[81] Nissan provided some specific driveability data in an effort to substantiate its driveability concerns, but the data provided were nevertheless insufficient to establish Nissan's contention that effective control technology is not available for its engine families. See the individual discussions of the driveability concerns of each applicant in Section VII of Appendix A.

[82] See, e.g. Sept. 12 TR., pp. 91-92 (testimony of Nissan).

[83] A comparison of fuel economy data between Toyo Kogyo vehicles designed to meet a 7.0 gpm CO standard and Toyo Kogyo vehicles attempting to meet a 3.4 gpm CO standard indicate that this penalty is somewhat smaller for manual transmission vehicles and changes to a significant fuel economy gain for automatic transmission vehicles. See Section VIII of Appendix A to this Toyo Kogyo also asserted that it could increase by 10 to 15 percent the fuel economy of its 1980 rotary engine certified in California below the 1981 Federal standards by replacing the thermal reactor system with an open loop three-way plus oxidation catalyst with air injection system. Toyo Kogyo cannot meet the 3.4 gpm CO standard, however, by using the open loop system. Because Toyo Kogyo already is marketing the thermal reactor system, I can only conclude that the fuel economy features of that system would not preclude Toyo Kogyo from marketing that system in a competitive manner in model year 1981.

[84] Sept. 12 Tr., p. 92.

investigations do not indicate that effective control technology, considering costs, driveability, and fuel economy, is not available for the engine families not receiving waivers. I also have made the same determination regarding the indications provided by other information available to me and included in the record. (See the discussion of "other information" in section III(B)(1)(c) of this decision).

2. *Protection of the Public Health.*—According to the requirements of section 202(b)(5)(C) of the Act, the Administrator must find that a waiver application has met each of the specified criteria with respect to a particular engine family before the Administrator may grant a waiver request. Thus, according to the express terms of the statute, there is no need for me to determine whether waiver applications covering engine families for which I am unable to determine that effective control technology, considering costs, driveability, and fuel economy, is not available to meet any of the remaining statutory criteria in order for me to deny these applications. Nevertheless, I am addressing these issues in this decision for the purpose of leaving as few matters as possible unresolved.

By the same reasoning I used in section III(B)(2) of this decision, I could conclude that the incremental ambient CO contributions from any engine family for which I have not determined effective control technology considering costs, driveability, and fuel economy, to be unavailable also is insignificant. In that case, waiving the 1981 and 1982 statutory CO standard for any one of those engine families arguably still would be protective of the public health.

As I already have noted, however, Appendix B projects that noticeable increases in CO levels could result from an industry-wide waiver under section 202(b)(5) of the Act. This result could hardly be protective of public health when the record indicates that as many as 189 urban areas measured violations of the CO NAAQS in 1978[85] and that studies project at least some 180 violations still to occur annually through 1985 in the 19 worst non-California, low-altitude AQCRs, even with a 3.4 gpm CO standard applied industry-wide beginning in the 1981 and 1982 model years.[86] By thus aggravating the detrimental health effects caused by violations of the CO NAAQS which studies already project will exist when 1981 and 1982 model year vehicles are in use, an industry-wide waiver of the 3.4 gpm CO emission standard would not be protective of public health.

Where granting waivers covering vehicles constituting only a small portion of the industry, however, would not create a significant effect on CO levels in non-attainment regions, or would not bring attainment regions into non-attainment, imposing the 3.4 gpm CO emission standard on these vehicles is not required to protect public health. Thus it is reasonable within the intent of section 202(b)(5)(C) to provide waivers on a limited basis by granting waivers covering only that portion of the industry consisting of engine families for which I have determined that effective control technology, considering costs, driveability, and fuel economy is not available (presuming these families also meet the remaining statutory criteria).

Nissan, as well as several applicants involved in the first set of CO waiver proceedings,[87] contended that recent measurements have shown a significant downturn in ambient CO levels which will lead to nationwide achievement of the CO NAAQS within an assertedly comparable time frame whether or not CO waivers are granted. Appendix B nevertheless indicates that an industry-wide waiver could measurably slow the progress towards the health-based CO NAAS in non-attainment areas. The longer an area is in non-attainment, the longer the public health lacks adequate protection.

Appendix B addresses the comments in the record challenging EPA's methodology in measuring and projecting ambient CO levels[88] and explains the reasoned basis for the EPA methodology employed to assess both ambient CO levels and the effects which granting these waiver requests may have.

Moreover, insofar as any comments submitted to the record have questioned the need for attainment of the 90 percent CO emission reduction requirement by the 1981 model year, the parties offering these comments have misconstrued Congress' intent in providing a CO waiver mechanism in the Act. Congress did not intend that I reassess the need for attaining the 90 percent reduction requirement by the 1981 model year to decide whether I should grant these waivers; rather, Congress included the public health consideration in section 202(b)(5)(C) of the Act to ensure that any waivers I granted, for a presumably limited number of engine families, would present no significant risk to the public health. In enacting section 202(b)(1) of the amended Act, Congress already had determined that considerations of public health adequately supported requiring the 90% reduction in CO emissions by the 1981 model year.

3. *Essential to the Public Interest or the Public Health and Welfare.*—I have determined that waivers for the engine families for which I have determined that effective control technology, considering costs, driveability, and fuel economy, is available are not essential to the public interest or to the public health and welfare.

On the basis of the information contained in the record, I conclude that in no case is granting a waiver essential to the public health and welfare. No applicant has made a claim that a waiver would enhance the public health and welfare, nor has any information supporting such a finding come to my attention. I have no basis for determining, for example, that manufacturers can achieve the statutory CO standard only at the risk of increasing emissions of other regulated or unregulated pollutants.[89] Thus, based on the information elicited for the record of the proceedings at hand, the scope of my examination of this issue narrows to whether a waiver is essential to the public interest.

Several applicants have stated that though their engine families may have some potential for meeting the 3.4 gpm CO emission standard, the engine families can achieve that emission level only by incurring extra costs (or fuel economy or driveability penalties) which the applicants could avoid under a less stringent CO standard.[90] These applicants contend that I should grant waivers covering these engine families because it is essential to the public interest to avoid any extra costs (or fuel economy or driveability penalties) relating to assertedly marginal improvements in ambient CO levels achieved by attainment of the 3.4 gpm CO standard.

This argument overlooks the purpose for which Congress included the CO waiver provision in the 1977 amendment to the Act. Congress obviously realized

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[85] Joint Comments from Environmental Defense Fund and National Resources Defense Council, p. 9 (July 30, 1979).

[86] EPA's Revised Air Quality Analysis of Waiving the 3.4 Grams/Mile CO Standard for Light-Duty Vehicles, dated August, 1979.

[87] See, e.g. C. App., I, p. C-3; GM App., p. 6.

[88] GM App., pp. 33–39. N. App., pp. 2.1–2.3. Ford also supplied specific comments on EPA's methodology. Ford, July 9, 1979, Attachment V. The applicants involved in this second set of CO Waiver proceedings have raised no new arguments in this area. See note 50, supra.

[89] EPA's Administrator made such a determination as part of the suspension proceedings for the 1977 model year motor vehicle exhaust emission standards because of his concerns regarding the uncertain health effects of possible increased sulfuric acid emissions. 40 FR 1190 (March 14, 1975).

[90] See, e.g., N. App., p. 1–5; TK App., p. 2.

that any 1981 model year vehicle model could attain the 90 percent reduction requirement for CO emissions, which it deemed ultimately necessary to achieve ambient CO levels protective of public health, only by incurring some extra cost, or perhaps some extra penalty to fuel economy or driveability. As noted earlier, however, Congress intended that waivers be granted on a limited basis only. Thus, it is highly unlikely that Congress envisioned the involvement of extra costs (or fuel economy or driveability penalties) alone as justification for granting a waiver request.

The public interest consideration at issue in these proceedings is whether adverse effects from any of these factors are substantial enough to present a significant risk that the applicant will not be able to produce and market competitively the engine family in question and perhaps other engine families as well. Section III(C)(1)(b) of this decision already has examined this aspect of the public interest consideration in discussing the effects of costs, driveability, and fuel economy on the availability of effective control technology.

My conclusion here parallels the one I reached there. Specifically, I have determined that it is not essential to the public interest to grant waivers to engine families which incur costs (or driveability or fuel economy penalties) in meeting the 3.4 gpm CO standard where the costs (or penalties) involved are not so substantial as to present a significant risk to the waiver applicant's ability to produce and market competitively vehicles of that engine family, or vehicles generally.

Fuji has claimed that it is further essential to the public interest that I grant its requested waivers to allow them to continue producing its four-wheel drive vehicles (constituting about half of its U.S. sales total).[91] Fuji explains that those vehicles offer added convenience and safety not available from most passenger vehicles when operated under poor driving conditions. I recognize that ensuring the availability of such special-purpose vehicles may benefit the public interest; however, I cannot determine that granting Fuji's requested waivers would actually help preserve the availability of these vehicles and thereby would be essential to the public interest. Because Fuji has not been able to establish that its engine families are not capable of meeting a 3.4 gpm CO standard, I cannot conclude that Fuji indeed will stop producing and marketing these special-purpose vehicles if it does not receive a waiver.

Renault stated that a waiver for its 85 CID engine family would serve the additional public interest of allowing it to market on a nationwide basis vehicles which meet California's stricter 1981 model year NO_x emission standard (0.7 gpm) and scheduled maintenance requirements.[92] In this case, however, Renault indicates that it can achieve improved NO_x emission levels only by sacrificing its ability to meet the CO emissions standards established by Federal law. By establishing the Act's schedule for required emissions reduction, Congress clearly indicated that it determined achievement of the 3.4 gpm CO standard more important to the national public interest than achievement of the emissions improvements in NO_x promised by Renault and required by California due to the state's unique pollution problems. Thus, I have determined that a waiver for Renault's 85 CID engine family would not be essential to the public interest for the reasons which Renault suggests.

4. *Good Faith.*—I already have addressed the good faith criterion in section III(B)(4) of this decision. My conclusion here for the engine families for which I have not determined that effective control technology, considering costs, driveability, and fuel economy, is unavailable is the same as my conclusion there. Specifically, I have determined that because the applicants for wiavers for these engine families have provided evidence supporting their good faith efforts to meet the 3.4 gpm CO standard and because the record contains no information providing any specific evidence to the contrary, I am unable to determine other than that these applicants have met the good faith criterion included in section 202(b)(5)(C)(ii) of the Act.

5. *Risks in Determining Available Technology*

In International Harvester Co. v. Ruskelshaus,[93].—the Federal appellate court reviewed the decision of EPA's Administrator to deny a set of applications for one-year suspension of the statutory 1975 model year light-duty motor vehicle emission standards, which included the 3.4 gpm CO standard. The criteria provided in the Act for the Administrator to make his decision were substantially similar to the criteria now provided in section 202(b)(5)(C) of the amended Act.[94]

Among other things, the court stated that the Administrator should have balanced the risk associated with erroneously denying the suspension requests versus the risk of erroneously granting them. In that proceeding, the court indicated that the balance should consider the economic costs (in terms of jobs and misallocated resources) possibly associated with an erroneous denial versus the possible environmental benefits lost through an erroneous grant.

On remand the Administrator reversed his previous decision and granted the suspension applications.[95] The Administrator cited as the most influenced factor in his decision the risk that introducing catalyst technology into mass production without a scale-up period of limited mass production could lead to severe economic disruption because of unanticipated difficulties (such as a manufacturer's inability to acquire a supply of acceptable catalysts). The Administrator stated that the one-year suspension of the statutory emission standards would give the industry an opportunity to gain experience in the limited mass production of catalyst-equipped cars under conditions of careful quality control while maintaining the accelerating momentum of progress in catalyst development that had occurred during the previous two years.

As part of the waiver proceedings at hand, applicants again have raised concerns over the risks they might face in being unable to implement effective control technology in mass production.[96] Today's circumstances, however, are substantially different from those that existed during the 1973 suspension proceedings.

At that time, the industry had no experience in producing vehicles incorporating catalyst technology; hence, the Administrator determined that the risks associated with implementing a new type of emission control system into production might indeed be significant. Since that time, however, the industry has gained a substantial amount of experience in the mass production techniques and quality control measures associated with catalyst-based emission control technology. The move from today's state of technology to the technology required to achieve the 3.4 gpm CO standard

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[91] Sept. 12 Tr., p. 104.

[92] R. App. P. III/1. Renault stated that if it received a waiver it would market a "50-state" 85 CID engine family which would meet all Federal and California emission requirements.

[93] 478 F.2d 615 (D.C. Cir. 1973).

[94] See the discussion of the 1970 version of the Act in Section I of this decision.

[95] 38 FR 1017 (April 26, 1973).

[96] See the discussion regarding applicants' risks and the establishing of design targets in section III(C)(1)(a) of this decision.

does not require any substantial shift to untried emission control methods. As a result, the uncertainties associated with that move now are much less than those associated with the initial move to catalyst technology.

Moreover, in the proceedings at hand I have made a separate determination regarding the availability of effective control technology, considering costs, driveability, and fuel economy, for each engine family covered by a wiaver application. The risks associated with requiring implementation of effective control technology for any one of these engine families are substantially smaller in scope than the risks associated with a determination that effective control technology is generally available for all vehicles of all manufacturers. An incorrect determination here regarding one (or even more than one) engine family will not necessarily prevent that manufacturer, or the industry as a whole, from being able to market other engine families for which effective control technology, considering costs, driveability, and fuel economy, is available to meet the applicable emission standards.[97] Also, a manufacturer may reapply for a waiver by submitting new information which was not available for consideration as part of these proceedings and which would further substantiate the applicant's claims.

In the proceedings at hand, therefore, I have determined for those engine families not receiving waivers that the risks of an erroneous denial of a waiver are justified when compared to the risks attendant to an erroneous grant. I have taken steps to minimize the risk of an erroneous denial by making sure that I base my findings that technology is available to meet certification testing requirements on conservative projections which themselves must demonstrate with no less than an 80% confidence level that vehicles of an engine family in question can pass a single certification test. I have found no information in the record which effectively corroborates the technology concerns raised by the applicants or other manufacturers, which have an obvious interest in a cautious assessment of their respective abilities to meet the 3.4 gpm CO standard.

Section III(B)(2) of this decision discusses the environmental health risks that would be associated with one or more erroneous grants. Even though the health risks associated with erroneous grants may not be great, the risks associated with erroneous denials (which do not involve health considerations) also are limited significantly. In addition, an erroneous grant would serve to discourage manufacturers from implementing available effective emission technology as quickly as possible. In light of these counterbalancing risks, and in light of Congress' expressed intent to afford a statutory waiver only in exceptional circumstances rather than on an across-the-board basis,[98] I have concluded that it is appropriate to deny waiver applications insofar as they cover engine families for which I have determined that effective control technology, considering costs, driveability, and fuel economy, is available.

6. *Conclusions.*—For the engine families referred to in section III(C) of this decision, I have determined either that effective control technology indeed is available for these 1981 model year engine families, even after considering costs, driveability and fuel economy, or that the waiver applicants have failed to provide adequate information to enable me to make a determination that technology is not available. Thus, even though the waiver applicants may meet one or more of the remaining statutory criteria for granting waivers, I nevertheless must deny the waiver applications covering these engine families.

iv. *Interim CO Exhaust Emission Standards*

As required by section 202(b)(5)(A) of the Act, I am simultaneously promulgating regulations prescribing interim CO emission standards for the 1981 model year vehicles of the two families, I am prescribing an interim CO emission standard of 7.0 gpm for both of these engine families. For these two engine families, this action continues in effect for one additional model year the CO emission standard applicable to all 1980 model year vehicles.

Dated: November 8, 1979.

Douglas M. Costle,
Administrator.

Appendix A.—Summary of Technological Capability

Contents

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I. Introduction

The exhaust emission standards for 1981 and later model year light-duty vehicles are currently 0.41 gram per mile HC, 3.4 grams per mile CO, and 1.0 gram per mile NOx. Section 202(b)(5)(A) of the Clean Air Act, as amended, 42 U.S.C. 7521 (b)(5)(A) provides the opportunity for manufacturers to request a waiver of the 3.4 grams per mile CO standard to 7.0 grams per mile during model years 1981 and 1982.

The applicants being considered in this document are Fuji, Nissan, Renault, and Toyo Kogyo. This is the second group of CO waiver applications that have been considered by EPA.

This appendix deals with the technological capability of those manufacturers to meet the 1981 and 1982 CO standard of 3.4 grams per mile. This appendix relies on three previous technical appendixes, particularly for discussion of the Monte Carlo simulation utilized in this analysis. These appendixes are:

1. Appendix B, Technical Appendix, to the Decision of the Administrator on Remand for the United States Court of Appeals for the District of Columbia Circuit, April 11, 1973.
2. Appendix A, Technical Appendix, to the Decision of the Administrator In re: Applications for Suspension of 1976 Motor Vehicle Exhaust Emission Standards, July 30, 1973.
3. Appendix A, Technical Appendix, to the Decision of the Administrator In re: Applications for Suspension of 1977 Motor Vehicle Exhaust Emission Standards, March 5, 1975.

As indicated in Section 202(b) (5) (iii), the technological feasibility determination is based on the consideration of technological capability, cost, driveability, and fuel economy. This appendix contains discussion of each of the above topics.

II. Summary of Technological Capability

Tables II–1 to II–4 summarize the capability of the four applicant

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[97] The risk that denial of a waiver request will cause significant harm to an applicant's ability to market vehicles in a competitive manner is substantially less with respect to these engine families, for which the record does not establish that effective control technology is not available, than is the risk with respect to the engine families for which the record demonstrates that technology is available. See the discussion of the public interest criterion in section III(B)(3) of this decision.

[98] While the previous statutory suspension provision directed the Administrator to reach a decision with respect to a manufacutrer in general, the current section 202(b)(5) directs the Administrator to examine separately the circumstances pertaining to each model (i.e. engine family). See also 123 Cong. Rec. S13702–13703 (Aug. 4, 1977) (remarks of Sen. Muskie).

manufacturers to meet the 1981 and 1982 emission standards. The standards considered in these tables are 0.41 HC, 3.4 CO, 1.0 NOx.

A guide to the summary tables is as follows. The first column lists engine displacement. The second column, which lists per cent of model year 1981 sales, is deleted because the values were derived in most cases from manufacturers' confidential sales estimates. The "as received" column refers to the emission data submitted by the manufacturer. "Improvements" refer to the projected technological improvements (factors) applied to the data submitted by the manufacturer.

The "no data" category is an abbreviated notation for the lack of acceptable data to perform EPA's technological analysis. The applicants have known for about six years what sort of data is necessary for EPA to make a determination whether or not a given vehicle would be projected to pass or fail a set of standards. Unfortunately, in many cases there was a lack of acceptable data for vehicles using specific engines. This effectively precluded EPA from making a pass/fail determination for those vehicles. In these cases the vehicles using these engines are called "no data" and no pass/fail determination was made.

Table II-1.—*Applicant: Fuji*

Engine	% estimated 1981 sales	Pass as received?	Pass with improvement?
97		No	Yes
109		No	Yes

Table II-2.—*Applicant: Nissan*

Engine	% estimated 1981 sales	Pass as received?	Pass with improvement?
75		Yes	N/A*
85/91		Yes	Yes
119		Yes	Yes
146/168		No	Yes
A		No Data	No data
B		No Data	No data

*N/A means not applicable or that improvements were not needed.

Table II-3.—*Applicant: Renault*

Engine	% estimated 1981 sales	Pass as received?	Pass with improvement?
85		No	Yes

Table II-4.—*Applicant: Toyo Kogyo*

Engine (CID)	% estimated 1981 sales	Pass as received?	Pass with improvement?
70 (Rotary)		Yes	N/A*
91		No	No in 1981 Yes in 1982
120		No	No in 1981 Yes in 1982

*N/A means not applicable or that improvements were not needed.

III. Statistical Treatment of the Data

No changes have been made in the basic Monte Carlo methodology since its last use in a technical appendix. This methodology has been discussed in three previous technical appendixes:

1. Appendix B, Technical Appendix, to the Decision of the Administrator on Remand for the United States Court of Appeals for the District of Columbia Circuit, April 11, 1973.
2. Appendix A, Technical Appendix, to the Decision of the Administrator In re: Applications for Suspension of 1976 Motor Vehicle Exhaust Emission Standards, July 30, 1973.
3. Appendix A, Technical Appendix, to the Decision of the Administrator In re: Applications for Suspension of 1977 Motor Vehicle Exhaust Emission Standards, March 5, 1979.

IV. Factors

With respect to the vehicle emission data submitted by the manufacturers for EPA analysis, vehicles are often run and tested over durability mileage accumulation schedules without using the best technology that is available to the manufacturer for certification in the 1981 model year. There are many reasons why this occurs. First, such technology may have simply not been available in quantity when fleets of vehicles began mileage accumulation. Second, all vehicles submitted for EPA staff analysis may not have been specifically designed for the 1981 and 1982 Federal emission standards. Also the manufacturer may wish to maintain some technologies (with known durability) in reserve if their low mileage testing indicates that such technology may not be needed for compliance with the target emission standards. In addition, technology may not appear on durability vehicles because the manufacturer has made a decision that the technology would be too costly for production vehicles.

To account for the fact that the applicants did not in all cases conduct durability testing with the most effective emission control hardware, factors, have been applied to some of the emission data submitted by the manufacturers, to simulate the addition of more effective systems. Due to substantial lead time problems for implementation of new or additional technology by the 1981 model year, these factors have been applied only for currently known hardware that can be implemented in 1981 certification and production. These improvements have been basically limited to additional catalyst (i.e., the addition of oxidation catalyst in some cases), the addition of air injection, and additional catalyst noble metal loadings. Other improvements in hardware were considered if the manufacturer indicated that they were available for 1981 and 1982.

The factors that have been applied to the data are dimensionless numbers that represent the improvement in emission performance that is predicted for the more effective simulated emission control technology. The factors are derived from data that reflect the emission performance of a vehicle with and without the more effective technology. For example, a factor for CO of 0.90 indicates that a 10 percent reduction in CO is projected for the use of the more effective technology. In addition, when there are several different sources for the same improvement, EPA uses a conservative estimate of that projected factor, i.e., a factor greater in absolute value than that indicated by most of the data.

Other factors which were developed, but generally not used in the following analysis include factors for:

- Deletion of power enrichment
- Use of insulated or dual-walled exhaust pipes
- Use of exhaust port liners
- Use of throttle body fuel injection
- Use of multiple point fuel injection
- High energy ignition

Although the deletion of power enrichment and the use of insulated or dual-walled exhaust pipes were considered feasible for 1981, they were generally not used (dual-walled exhaust pipes were utilized for one engine family in Nissan). Therefore, through these additional techniques, the manufacturers may have some additional cushion for certification over and above the factors used in EPA's analysis. Use of the other items was not considered possible for most manufacturers for most engine families before the 1982 model year.

Duel-Walled Exhaust Pipe Factor (Nissan)

This factor was applied to Nissan vehicles using 119 CID engines and FB/PAIR/EGR/OC emission control systems.

The data used to develop this factor were presented by Nissan [19 at 15 to

17] * and repeated here in Table IV–1. Other data were available from GM and Chrysler. However, the data used are for the specific engine in question.

The derived factors are supported by the GM and Chrysler data [20 at, Volume IIIB, vehicle 305, tests 30 & 31] [21 at 7–139] [22] which if averaged for the three sets of data would yield factors of 0.85 for HC, 0.74 for CO, and 1.01 for NOx.

Nissan has stated that this technology will be avilable for this particular engine (and additional engines) in 1981 if needed [13 at section IV, p. 13].

No fuel economy impact was noted as seen in the table.

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* [19 at 15 to 17] is a compact notation used to mean that the reference being cited is reference 19 (from the reference list at the end of this appendix) at pages 15 to 17.

Table IV–1.—*Development of the Nissan Factors for Dual-Walled Exhaust Pipes*

VIN	IW	Eng	Trans	Axle	Emission control system	75 FTP				Comments
						HC	CO	NOx	MPG$_u$	
BK579	2875	119	M5	3.700	EFI/EGR/PAIR/OC	.284	1.58	1.62	27.6	Base.
						.256	1.30	1.75	27.5	With dual-walled exhaust pipe.
					Factor	0.90	0.82	1.08	1.00	

Improved Oxidation Catalyst (Nissan)

These factors were used in the computer simulation of the Nissan vehicles using 119 CID engines and FB/PAIR/EGR/OC emission control systems (vehicles BK649, B1968, 8D–991, and 8D–992).

The data from which these factors were developed were taken from Nissan vehicle BK576 [13 at 5 to 6]. This vehicle was almost identical to the vehicles to which the factors were applied except that it used EFI as opposed to carburetion. These data are reproduced here in table IV–2. Both catalysts were aged 50,000 miles.

Nissan stated that the improved catalyst will be available for the 1981 model year [5 at 55–56], and as expected, no adverse impact on fuel economy was found.

Table IV–2.—*Nissan Factors for Improving Oxidation Catalyst for Vehicles Having 119 CID Engines*

VIN	IW	Eng	Trans	Axle	Emission control system	75 FPT				Comments
						HC	CO	NO$_x$	MPG$_u$	
BK576	2875	110	M5	3.700	FB/EFI/EGR/PAIR/OC	.361	2.58	0.77	27.5	Base case.
						.331	2.32	0.78	27.4	With improved catalyst.
					Factor	0. 92	0.90	1.01	1.00	

Recalibration of Ignition Timing During Cold Start (Nissan)

This factor was utilized in the Monte Carlo analysis of Nissan vehicles using 85 and 91 CID engines with AIR/EGR/OC emission control systems.

Data for this recalibration on vehicle K110 using the 91 CID engine were presented by Nissan [13 at V to 18]. The data are presented here in table IV–3. All tests in this table were conducted with the same vehicle with a catalyst aged to 50,000 miles.

As this is only a recalibration, it does not present a lead time problem for model year 1981. Fuel economy was essentially unaffected by this recalibration.

Table IV–3.—*Recalibration of Ignition Timing During Cold Start*

VIN	IW	Eng	Trans	Axle	Emission control system	75 FPT				Comments
						HC	CO	NOx	MPG$_u$	
K110	2375	90.8	M4	3.700	AIR/EGR/OC	.300	4.03	0.70	30.1	Base.
						.259	3.48	0.68	30.2	Base.
						.280	3.76	0.69	30.2	Average base.
						.252	2.21	0.69	30.1	With timing recalibration for quick catalyst light-off.
						.244	3.04	0.68	29.9	Repeat.
						.248	2.62	0.68	30.0	Average with recalibrated timing.
					Factor	0.89	0.70	0.99	1.00	

Factors for a Clean Up Oxidation Catalyst With a Switched AIR System

The EPA technical staff considers the FBC/3W/OC/EGR/Switched AIR emission control system to be the most promising means to achieve the 1981–1982 emission standards.

Several manufacturers have selected emission control systems using only FBC/3W/EGR as their first choice control system for compliance with the 1981–1982 emission standards. Because several of these manufacturers have run durability vehicles using only the FBC/3W/EGR system, the EPA technical staff has developed a hardware improvement factor for the addition of a clean up oxidation catalyst with a switched AIR system.

The factors used in Monte Carlo to stimulate a clean up oxidation catalyst and switched AIR system were 0.60, 0.40 and 1.40 for HC, CO and NOx respectively. These factors were developed from data supplied by British Leyland [35 at 26] and Matthey Bishop [42 at Tables III & IV and 28 at Table V], and are shown in Table IV–4. The significant emission control improvement afforded through the use of this hardware is expected to aid the manufacturers in optimizing calibrations for fuel economy and driveability.

The British Leyland data are in gms/mile, whereas the Matthey Bishop data are for catalyst conversion efficiencies. The formulas used to calculate the British (BL) and Matthey Bishop (MB) factors are as follows:

$$\text{BL Factor} = \frac{\text{gms/mile}_{(3w+oc)}}{\text{gms/mile}_{(3w)}}$$

$$\text{MB Factor} = \frac{1-\eta_{(3w+oc)}}{1-\eta_{(3w+oc)}}$$

where η is catalyst efficiency expressed as a decimal

Table IV–4.—*Data Used to Derive Factors for the Addition of Air Injection and an Oxidation Catalyst*

	HC	CO gms/mile*	NO_x
British Leyland—3W	0.16	2.69	0.14
BL—3W+OC	0.31	0.73	0.4
BL Factor for OC & Switched AIR	0.81	0.27	2.86
	Conversion Efficiency (percent)		
	HC	CO	NO_x
Matthey Bishop Data—VIN, Catalyst and Simulated Miles:			
8B438, 3W(A)**, 4K miles	78	66	67
61E37, 3W(A)+OC, 4K miles	92	92	70
MB Factors for 3W(A)+OC at 4K miles	0.36	0.24	0.91
8B438, 3W(A), 50K miles	80	59	64
61E37, 3W(A), 50K miles	91	93	66
MB Factors for 3W(A)+OC at 50K miles	0.45	0.17	0.91
8B438, 3W(B)**, 4K miles	82	75	74
61E37, 3W(B)+OC, 4K miles	92	95	75
MB Factors for 3W(B)+OC at 4K miles	0.44	0.20	0.96
8B(B), 3W(B), 50K miles	79	65	65
61E37, 3W(B)+OC, 50K miles	89	91	63
MB Factors for 3W(B)+OC at 50K miles	0.52	0.26	1.06
Average of Factors for adding a Clean Up Oxidation Catalyst and Switched AIR System	0.52	0.23	1.16
Factors Used in Monte Carlo	0.60	0.40	1.40

*Factors are dimensionless

**Matthey Bishop included data on two three-way catalysts which are identified as 3W(A) and 3W(B).

In order to equally weight each test point, the following formula was used to calculate the average factor:

Average Factor = [BL Factor + MB 4K(A Factor) + MB 50K(B Factor) + MB 4K(B Factor) + MB 50K(B Factor)] ÷ 5

The vehicle descriptions [36 at 1] for the two vehicles used to generate the Matthey Bishop data are as follows:

Vehicle 61E37—Pinto 2.3L, 2750# I.W., PAU 9.9
Catalyst—3W+OC
Carburetor—2V FBC with closed loop control at idle
EGR—vacuum/back pressure with electrical closure at idle and WOT
Air Pump—air upsteam at cold start, switched to mid-bed at 128°F water temperature
Spark Advance—mechanical
Oxygen Sensor for FBC
Electronics—FBC trim control only

Vehicle 8B438—Fairmont 2.3L, 3000# I.W., PAU 11.3
Catalyst—3W only
Fuel System—Bosch L Jetronic with closed loop WOT
EGR—vacuum/electric control
No air pump
Spark Advance—mechanical
Oxygen Sensor for FBC
Electronics—full fuel control

The British Layland vehicle description is as follows:

2750 lb. test weight
120 cubic inch engine
feedback fuel injection
EGR

No further details were provided by British Layland.

The data in Table IV–5 were used to help determine the validity of the factors used in the Monte Carlo. This is a table of factors calculated from data supplied by Chrysler [32 at Volume IIIA]. The Chrysler data were not used to determine the Monte Carlo factors because the Chrysler factors are calculated from tailpipe and three-way catalyst-out emissions on vehicles with a switched AIR system. Obviously, such data can not be used for the development of this factor, but it did indicate that the general trend of the data does agree with the factors used in the Monte Carlo analysis.

This factor was used on some vehicles from all the current applicants except Nissan.

Table IV–5.—*Chrysler Factors*

Car ID No.	HC	CO	NO_x	Test points [1]
485	.43	.40	1.21	8–20
131H	.42	.38	1.00	12–29
162H	.47	.44	.87	9–17, 22–30
166	.44	.39	1.40	Unnumbered
311	.50	.55	1.03	8–20
537	.39	.23	1.50	38–41, 43–48
Average factors	.44	.40	1.17	
Factors used in Monte Carlo.	.60	.40	1.40	

[1] Durability test points only.

Clean Up Oxidation Catalyst With Aspirator Factor

As discussed in the prior section, a clean up oxidation catalyst with a switched AIR system is very effective in controlling HC and CO. Most of the manufacturers using a three-way catalyst followed by an oxidation catalyst employ a switched AIR system to supply additional oxygen to the inlet of the oxidation catalyst. Volkswagen has taken a new approach by using an aspirator to supply air to the inlet of the oxidation catalyst [32 at 4.21].

Unlike a switched AIR system, Volkswagen's "between catalyst aspirator" does not supply air to the exhaust ports during warm up, and therefore would theoretically be less effective for HC and CO control. The data submitted to EPA [32 at 5.14, 5.17, and 5.19] indicates that the HC reduction for Volkswagen's clean up oxidation catalyst with an aspirator exceeds the HC reduction shown in the Matthey Bishop data [44 at Tables III & IV and 45 at Table V] and British Leyland data [35 at 26] for a clean up oxidation catalyst with a switched AIR system. The factors used in the Monte Carlo, 0.70, 0.55 and 1.50 for HC, CO and NOx respectivey, reflect the EPA technical staff's judgment that a switched AIR system would, in most cases, be more effective in oxidizing HC and CO than an aspirator system, and therefore the HC factor was adjusted accordingly.

Volkswagen presented durability data on two vehicles with dual-bed catalysts and aspirators, and four vehicles with single-bed three-way catalysts. One vehicle with the dual-bed, and two vehicles with the single-bed catalyst were not used in determining the factors because they had deterioration factors for CO of less than one, which is not typical and is an indicator that the air/fuel ratio may have been getting leaner with mileage accumulation. The factors, and data used in developing the factors are presented in Table IV–6.

This factor was applied only to vehicles submitted by Fuji, who has claimed that due to space restrictions, heat shielding for a clean up oxidation catalyst could not be added [3 at 117 to 121]. After reviewing the photographs provided in an effort to substantiate their claims, the EPA technical staff can not agree with Fuji's assessment of the situation and is of the judgment that a clean up oxidation catalyst with an aspirator between the catalysts is a viable alternative for Fuji.

Table IV-6.—*Aspirator Plus Oxidation Catalyst Factors*

VIN and catalyst	Average of extrapolated 4K and 5K values (gm/mile *)		
	HC	CO	NOx
439-517—3W only	0.75	10.68	0.53
439-611—3W only	0.41	11.45	1.15
Average Emissions for 3W Catalyst Vehicles	0.58	11.07	0.84
449-528—3W + OC with Aspirator between catalysts	0.24	5.35	1.22
Factors as calculated for Clean Up OC with Aspirator instead of 3W only	0.41	0.48	1.45
Factors as Used in Monte Carlo for Clean Up CO with Aspirator between catalysts	0.70	0.55	1.50
Factors as Used in Monte Carlo for Clean Up OC with Switched AIR**	0.60	0.40	1.40

* Factors are dimensionless.

** See discussion of Factors for Clean Up OC with Switched AIR.

Fuji Catalyst Improvement Factors

Fuji presented catalyst efficiency data and catalyst specifications which the EPA technical staff used to develop a catalyst improvement factor. Because the catalyst specifications are confidential, the following discussion is absent such information.

Fuji vehicle A22–347985 and A33–061901 use catalysts A1 and A2 respectively. Catalysts A6 and A7 are improved catalysts which Fuji has recently included on new durability vehicles. Also, catalyst A1 should have been more active than catalyst A2. The catalyst efficiency data shown in Table IV–7 indicated minor discrepancies, that, in the judgement of the EPA technical staff, arise from the fact that engine-out emissions and tailpipe emissions were not read simultaneously. For instance, at 500 hours, catalyst A7 showed a lower CO conversion efficiency than catalyst A1, and at 300 hours, catalyst A2 showed a higher HC efficiency than catalyst A1.

Because these discrepancies may have been due to the variability caused by the approach discussed above, the technical staff judged that the data would be more meaningful if an average of the conversion efficiencies of A1 and A2 were compared to an average of the A6 and A7 conversion efficiencies. This would result in a more valid indication of the improvement which can be expected through the use of improved catalysts.

The formula used to calculate the catalyst improvement factor for each pollutant is as follows.

$$\text{Factor} = 1 - \frac{\eta_{A6} + \eta_{A7}}{2} \div 1 - \frac{\eta_{A1} + \eta_{A2}}{2}$$

where η is catalyst efficiency expressed as a decimal.

As shown in Table IV–7, the catalyst improvement factors used in the Monte Carlo analysis were 0.80, 1.00 and 0.60 for HC, CO, and NOx respectively. Because 500 hour data were not submitted for catalysts A2 and A6, 500 hour data were not used in the factor calculation. Zero hour data were also not included because they are not included in deterioration factor calculations and are generally not useful in analyzing data.

Table IV-7.—*Fuji Catalyst Improvement Factors*

Catalyst	Conversion Efficiency 300 hrs of Aging (percent*)			Catalyst Efficiency 500 hrs of Aging (percent*)		
	HC	CO	NOx	HC	CO	NOx
A1	87.5	69.4	66.8	85.2	67.4	64.3
A2	88.6	66.7	72.4			
Average Efficiency for A1 & A2	88.05	68.05	69.6			
A6	91.2	70.6	82.6			
A7	91.3	70.3	84.3	90.0	62.7	77.4
Average Efficiency for A6 & A7	91.25	70.45	83.45			
Factors as calculated for A6 & A7 instead of A1 & A2	0.73	0.92	0.54			
Factors as Used In Monte Carlo for Catalyst Improvement	0.80	1.0	0.60			

*Factors are dimensionless.

AIR System Factors With 3-Way Catalysts

The factors for the addition of warm-up air injection (AIR) used in the Monte Carlo were 0.8, 0.8 and 0.95 for HC, CO, and NOx respectively.

The factors used for warm-up AIR as a replacement for warm-up pulse or reed valve air injection (PAIR) were 1.00, 0.90 and 1.00.

"To date the most successful exhaust treatment technique used commercially has been air injection into the exhaust system" [18 at 210]. Although this claim is now outdated, it does indicate that significant emission reductions are possible with the addition of an AIR System.

Data from Volvo [24 at 4–39] and Saab [25 at Enclosures 2 and 5] were used in calculating the factor for the addition of warm-up AIR.

The data from Saab Enclosure 5 shows the influence of AIR vs. no AIR on Bag 1 CO results only. In order to translate this data into FTP results, the following formula [26 at 32988] was used:

$Ywm=(0.43\ Yct+0.57\ Yht+Ys)/7.5$

Where:

Ywm = Weighted mass emissions of each pollutant, i.e. HC, CO, or NOx, in grams per vehicle mile.

Yct = Bag 1 = Mass emissions as calculated from the "transient" phase of the cold start test, in grams per test phase.

Yht = Bag 3 = Mass emissions as calculated from the "transient" phase of the hot start test, in grams per test phase.

Ys = Bag 2 = Mass emissions as calculated from the "stabilized" phase of the cold start test, in grams per test phase.

Enclosure 2 of the Saab subpoena submittal is a table of "Selected Bag Results From Various MY80 Certification Tests" which includes data from a turbocharged engine. The averages of twelve tests are as follows:

Yct = Bag 1 = 43.09 grams CO

Ys = Bag 2 = 5.68 grams CO

Yht = Bag 3 = 8.23 grams CO

$Ywm=[0.43\ (43.09)+0.57\ (8.23)+5.68]/7.5$

$Ywm=3.85$ grams/mile CO

Saab enclosure 5 shows the influence of air injection on CO in Bag 1 at 4,000 miles and at 50,000 miles for a turbocharged engine.

At 4,000 miles, Bag 1 CO was reduced by 11 grams, which when subtracted from Yct, gives 32.09 grams CO in Bag 1 for an AIR equipped engine.

Ywm equals 3.22 grams/mile for the AIR equipped vehicle at 4,000 miles.

At 50,000 miles the bag 1 results were reduced by 18 grams, giving 25.09 grams CO in Bag 1.

Ywm at 50,000 miles* equals 2.82 grams/mile CO.

The average of the 4,000 mile and 50,000 mile emissions is as follows:

Ywm w/AIR

$=(Ywm\ 4K)+(Ywm\ 50K)/2$

$=(3.22+2.82)/2$

$=3.02$ grams/mile CO with AIR

Ywm no/AIR = 3.85 grams/mile CO as calculated previously

The AIR System Factor is:

$$\text{AIR System Factor for CO}=\frac{\text{Ywm w/AIR}}{\text{Ywm no/AIR}}$$

$$=\frac{3.02}{3.85}$$

AIR System Factor for CO = 0.78

The Volvo-Saab data are combined in Table IV–8.

Table IV–8

Vehicle	Gms/mi*		
	HC	CO	NOx
Volvo, no/AIR	0.19	2.85	0.14
KMU 748 Auto, w/AIR	0.15	2.36	0.13
Factor-AIR	0.79	0.83	0.93
Volvo, no/AIR	0.21	2.79	0.11
KFL 989-Manual, w/AIR	0.15	2.16	0.10
KFL 989-Manual, w/PAIR	0.15	2.43	
Factor-AIR (as calculated)	0.71	0.77	0.91
Factor-PAIR vs no/AIR (as calculated)	0.71	0.87	
Factor-AIR vs PAIR (as calculated)	1.00	0.89	
Saab Turbo, no/AIR		3.85	
Saab Turbo, w/AIR		3.02	
Factor-AIR (as calculated)		0.78	
Factor-AIR (avg-Volvo + Saab) (as calculated)	0.75	0.79	0.92
Factor as Used in Monte Carlo AIR vs no AIR	0.80	0.80	0.95
Factor as Used in Monte Carlo-AIR vs PAIR	1.00	0.90	1.00

*Note: Factors are dimensionless.

V. Discussion of Individual Manufacturer's Technical Capability

This section will discuss all vehicles which (1) were submitted by each of the four applicants and (2) also are acceptable for input into the Monte Carlo simulation. Acceptable for input means (1) that the vehicle is a durability vehicle which has accumulated a minimum of 20,000 miles with the same major emission control components and (2) that a minimum of four valid 1975 FTP tests have been conducted on the vehicle.

Details of the pass/fail determinations in Section II are also presented here. To pass the 1981 and 1982 emission standard (of 0.41 HC, 3.4 CO, 1.0 NOx), the probabilities of passing each individual pollutant must be greater than or equal to 80%. If the probability of passing only HC for example, is less than or equal to 79%, the vehicle fails—even if the probabilities for CO and NOx greatly exceed the 80% cutpoint.

Due to time constraints for this analysis, pass/fail analysis is provided only for emission standards of 0.41 HC, 3.4 CO and 1.0 NOx. Analysis of the capability of the vehicles to meet the standard of 0.41 HC, 7.0 CO, 1.0 NOx were not conducted. Consequently, vehicles designed for a 7.0 CO standard are included in the following discussions of vehicles which were acceptable for entry into the computer analysis, but are not discussed with respect to compliance at 7.0 CO.

In order that the Monte Carlo analysis not be cluttered with hundreds of failing vehicles utilizing inappropriate technology, prior certification vehicles are not considered in this analysis except in special cases where a manufacturer's ability to comply with the 1981 and 1982 emission standards is directly affected. It is not surprising that the durability vehicles from past certification would fail to achieve the 3.4 CO standard for two reasons. First, this standard represents a substantial reduction in CO from prior model year standards. And second, major changes in technology are being planned for introduction in 1981 by most vehicle manufacturers to achieve the more stringent standards.

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* This is not to say that 50,000 mile emissions for an AIR System would be lower than 4,000 mile emissions. It does, however, indicate the emissions reduction from a given baseline with an AIR System.

If a manufacturer's prime (prime means the system most capable of achieving the 1981 standards) 1981 emission control system has been tested in prior certification (generally 1980), these data are included in the analysis.

Fuji

Fuji has requested a waiver for vehicles using the 97 CID and the 109 CID engines. Fuji's first choice emission control system for vehicles using both engines includes feedback carburetion, a three-way catalyst and exhaust gas recirculation (FBC/3W/EGR). Table V–1 lists the durability vehicles that Fuji included in their waiver application.

In addition to vehicles with their first choice system, Fuji has also included vehicles with their SEEC–T control system, which consists of pulse-air injection, insulated exhaust manifolds and exhaust gas recirculation (PAIR/IEM/EGR), and vehicles with their oxidation catalyst system which consists of pulse-air injection, an oxidation catalyst and exhaust gas recirculation (PAIR/OC/EGR). Because Fuji's three-way catalyst control system is the only one designed to meet the 1981–1982 standards, only those vehicles so equipped were considered in the pass/fail analysis for each engine.

The EPA technical staff has added numerical suffixes to Fuji's VIN's to aid in identifying vehicles with and without factors. Vehicles will be discussed by Fuji's VIN, but Table V–2 and the Monte Carlo printouts include the suffixes added by EPA. EPA has also added alphabetic suffixes to distinguish between different vehicles which Fuji has submitted with identical VIN's. The alphabetic suffixes added by EPA are included throughout appendix A.

Table V–1

Engine	VIN*	Emission control system**	Entered in Monte Carlo	If not entered in Monte Carlo, why?	References***
109	80CD–C	PAIR/IEM/EGR	Yes		FWA p. A–6–1
97	80CD–D	PAIR/IEM/EGR	Yes		FWA p. A–6–2
97	80FD–B	PAIR/OC/EGR	Yes		FWA p. A–7–1
109	A66L–617992–A	PAIR/OC/EGR	Yes		FWA p. A–7–2
97	A22–347985	FBC/3W(A1)/EGR	Yes		FWA p. A–8–1
109	71A–1446–A	FBC/3W(A1)/EGR	Yes		FWA p. S–8–2
97	A26L–671177	FBC/3W(A1)/EGR	No	Insufficient Data	FAI p. S–5–1
97	A67L–503419	FBC/3W(A1)/EGR	No	Insufficient Data	FAI p. S–5–2
97	A33–061901	FBC/3W(A2)/EGR	Yes		FAI p. S–5–3
109	A66L–617992–B	FBC/3W(A5)/EGR	Yes		FAI p. S–5–4
109	71A–1146–B	FBC/3W(A5)/EGR	No	Insufficient Data	FAI p. S–5–5
97	A26L–67497	FBC/3W(A6)/EGR	No	Insufficient Data	FAI p. S–5–6
109	76T–2128	FBC/3W(A6)/EGR	No	Insufficient Data	FAI p. S–5–7
109	76T–2128	FBC/3W(A7)/EGR	No	Insufficient Data	FAI p. S–5–8
109	A33–037049	FBC/3W(A7)/EGR	No	Insufficient Data	FAI p. S–5–9

* Vehicles with duplicate VIN's have a suffix added by EPA.

** Three way catalysts include identification designation (e.g. 3W(A1)).

*** FWA is used here as an abbreviation for reference 3.

FAI is used here as an abbreviation for reference 16.

Table V–2.—*Monte Carlo Results of Fuji Vehicles With FBC/3W/EGR*

VIN	Engine	Catalyst*	Probability of Pass			Comments
			HC	CO	NO_x	
A22–347985	97	A1	69	6	100	No Factors
A22–347985–2	97	A1	100	86	100	Factors for Catalyst Improvement and OC + Aspirator
A22–347985–3	97	A1	100	96	100	Factors for Catalyst Improvement and OC + Switched AIR
A33–061901	97	A2	46	1	97	No Factors
A33–061101–2	97	A2	98	77	99	Factors for Catalyst Improvement and OC + Aspirator
A33–061901–3	97	A2	99	96	100	Factors for Catalyst Improvement and OC + Switched AIR
A22+A33	97	(A1–A2)	49	18	99	2-Car Analysis—No Factors
A22+A33–2	97	(A1–A2)	100	85	100	2-Car Analysis—Factors for Catalyst
			99	87	100	Improvement & OC + Aspirator
A22+A33–3	97	(A1–A–2)	100	96		2-Car Analysis—Factors for Catalyst Improvement & OC + Switched AIR
71A–1446–A	109	A1	87	2	87	No Factors
A66L–617992—B	109	A5	100	25	100	No Factors
A66L–617992–B–2	109	A5	100	94	83	Factors for OC + Aspirator
A66L–617992–B–3	109	A5	100	99	94	Factors for OC + Switched AIR

* See Pass/Fail Analysis for the Fuji 97 CID Engine Family for explanation of (A1–A2).

Pass/Fail Anaylsis for the Fuji 97 CID Engine Family

Vehicles using the 97 CID engine are predicted to pass with either one of the two following combinations of hardware improvement factors:

(a) An improved three-way catalyst and a clean up oxidation catalyst with an aspirator between the catalysts, and

(b) An imrproved three-way catalyst and a clean up oxidation catalyst with a swtiched AIR system.

Vehicles with this engine are projected to fail without hardware improvement factors. Table V–2 lists the Monte Carlo results of Fuji vehicles equipped with the FBC/3W/EGR system, which is Fuji's only emission control system currently designed to meet the 1981–1982 standards. Vehicles with their SEEC–T and PAIR/OC/EGR systems were therefore not included in this analysis.

Vehicles A22–347985 and A33–061901 were run with and without factors, and both a one-car analysis and a two-car analysis were done. A one-car analysis is the standard analysis used in the CO Waiver Decision of September 5, 1979 and will not be further explained. Vehicle A22–347985 passed the one-car analysis with factors and failed without factors. Vehicle A33–061901 failed the one-car analysis with and without factors.

A two-car analysis includes the results of two identical durability vehicles as is sometimes done for certification. In the two car analysis, both vehicles passed with factors. These vehicles are not considered identical without factors because A22–347985 was equipped with catalyst A1 and vehicle A33–061901 was equipped with catalyst A2. With factors for hardware improvements, they are considered to be identical.

As explained in the discussion of the Fuji catalyst improvement factor, catalysts A1 and A2 were averaged because, although A1 should have been a more active catalyst, in some cases its conversion efficiencies were lower than those of A2. The unexpected results may be attributable to Fuji's test procedure rather than catalyst capability or potential. Engine-out emissions and tailpipe emissions were not measured simultaneously. Test variability associated with separate tests could have caused the inconsistencies, especially if the results were based on one test in each configuration rather than an average of several tests. Fuji did not indicate the number of tests performed.

The vehicle identification numbers for the two vehicles in the two-car analyses are A22+A33-2 and A22+A33-3 for the hardware improvement factor cases, and A22-A33 for the without factors case. As combined vehicles in the two-car analyses, A22-347985 and A33-061901 failed without factors and passed with hardware improvement factors. The specific improvements are enumerated in Table V-2. Based on the results of these two-car analyses, this family is projected to pass with either one of the improved emission control systems.

Pass/Fail Analysis for the Fuji 109 CID Engine Family

The 109 CID engine family is predicted to pass with either one of the two following hardware improvement factors; (a) a clean up oxidation catalyst with an aspirator between the catalysts, or with (b) a clean up oxidation catalyst with a switched AIR system. This family is projected to fail without improvements.

The Monte Carlo results are listed in Table V-2 for vehicles with the FBC/3W/EGR control systems. As explained in the Pass/Fail analysis for the 97 CID engine family, vehicles with control systems not currently designed to meet the 1981-1982 standards were not included in this analysis.

The projections for this family are based on the results of vehicle A66L-617992-B. This vehicle was unique in that it was the only durability vehicle with Fuji's catalyst warm up system. It was also the only Fuji durability vehicle using the A5 catalyst which met the minimum criteria for inclusion in the Monte Carlo analysis. Although all of the other durability vehicles with 109 CID engines and sufficient data for inclusion in the Monte Carlo failed the simulation, they were equipped with the FBC/3W(A1)/EGR system or other less advanced emission control systems. Therefore, A66L-617992-B, with either one of the two hardware improvements discussed above, is considered by the EPA technical staff to be representative of Fuji's capability to comply with the 1981-1982 emission standards.

Nissan

Nissan has requested a waiver for several engine families in model year 1981. Two distinct groups of technology have been identified by Nissan. One group will be used if a waiver to 7.0 CO is granted and the second group of technology will be used if compliance with 3.4 CO is required.

There have been no real durability vehicle fleets run by Nissan to aid in analysis of their ability to certify in 1981. In fact, only two of the durability vehicles that were eligible for Monte Carlo analysis were designated as being targeted for 1981 Federal emission standards. Those were vehicles A612 with a 91 CID engine and F671 with a 168 CID engine. The remainder of the vehicles presented by Nissan are typically 1980 California certification or development vehicles (designed for .41 HC, 9.0 CO, 1.0 NOx) or vehicles from their low NOx research program (designed for 0.41 HC, 3.4 CO, 0.41NOx).

Emission data from a large number of vehicles were presented in the Nissan waiver application documents as shown in table V-3. Unfortunately, most of the vehicles were development vehicles and did not accumulate a sufficient number of test points or sufficient mileage for entry into the EPA Monte Carlo analysis.

Table V-3.—*Vehicles in Nissan Waiver Application*

Engine	VIN	Emission control system	Entered in Monte Carlo?	If not entered in Monte Carlo—Why?	Comment	Reference[1]
119	YD021	EFI/FB/light EGR/3W.	Yes		Available for 1981.	NWA, p. 4.3.3.
119	YD020	FBC/FB/light EGR/3W.	Yes		Not available for 1981.	NWA, p. 4.3.3.
108	B2007	PAIR/EGR/OC (+OSC in some tests).	No	Waiver not requested		NWA, p. 4.6.7.
108	B1967	PAIR/EGR/OC (+OSC in some tests).	No	Waiver not requested		NWA, p. 4.6.8.
168	F671	EFI/EGR/3W (+3WSC in some tests).	Yes, with start catalyst.	Insufficient number of test points without start catalyst.		NWA, p. 4.6.9.
168	8D-645C	EFI/3W (1.7l cat).	Yes	Called 8D-645CB		NWA, p. 4.6.13 +, NSSS, p. 7.
168	8D-645C	EFI/3W (2.5l cat).	Yes	Called 8D-645CA		NWA, p. 4.6.13, NSSS, p. 7.
119	B2136	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.1-2.
119	#265	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.1-2.
119	B2075	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.1-2.
119	BK577	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.5, NSS, p. 17-18.
119	AK687	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.5.
119	BK585	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.5.
119	AK860	FB/PAIR/EGR/OC.	No	Insufficient number of data points		NWA, p. A.IV.5.
90.8	AK714	AIR/EGR/OC	No	Recalibration between tests		NWA, p. A.IV.10-10a, NSA, p. 9.
90.8	AK618	AIR/EGR/OC	No	Recalibration between tests		NWA, p. A.IV.12-12a.
168	F780	EFI/3W	No	Recalibration between tests		NWA, p. A.IV.14-14a, NSA, p. 25.
119	BK649	FB/PAIR/EGR/OC.	Yes		1980 calibration certificate.	NWA, p. A.IV.16, NSA, Response #3.

Table V-3.—*Vehicles in Nissan Waiver Application*—Continued

Engine	VIN	Emission control system	Entered in Monte Carlo?	If not entered in Monte Carlo—Why?	Comment	Reference[1]
119	8D-992	FB/PAIR/EGR/OC.	Yes		1980 calibration development.	NWA, p. A.IV.18, NSA, Response #3.
119	8D-991	FB/PAIR/EGR/OC.	Yes		1980 calibration development.	NWA, p. A.IV.20.
119	B1968	FB/PAIR/EGR/OC.	Yes		1980 calibration development.	NWA, p. A.IV.22.
119	AK690	FB/EFI/PAIR/EGR/OC.	Yes		1980 calibration certificate.	NWA, p. A.IV.24.
119	BK584	FB/EFI/PAIR/EGR/OC.	Yes, using data up to recalibration.		1980 calibration development.	NWA, p. A.IV.26.
119	BK578	FB/EFI/PAIR/EGR/OC.	Yes		1980 calibration development.	NWA, P. A.IV.28.
85.2	AK749	AIR/EGR/OC.	Yes		1980 calibration certificate.	NWA, p. A.IV.30.
75.4	A883	AIR/EGR/OC.	Yes		1980 certificate.	NWA, p. A.IV.32.
90.8	A555	AIR/EGR/OC.	Yes		1980 development.	NWA, p. A.IV.34.
85.2	A609	AIR/EGR/OC.	Yes		1979 development.	NWA, p. A.IV.36.
168	F836	EFI/3W	Yes		1980 calibration certificate.	NWA, p. A.IV.38.
168	F675	EFI/EGR/3W	Yes		1980 calibration development.	NWA, p. A.IV.40.
168	F614	EFI/EGR/3W	Yes		1980 calibration development.	NWA, p. A.IV.42.
119	CB516	FB/PAIR/EGR/OC.	No	Changes in hardware and calibration changes between tests.	1981 development.	NSA,[2] p. 1.
119	CB514	FB/PAIR/EGR/OC.	No	Changes in hardware and calibration changes between tests.	1981 development.	NSA, p. 3.
119	BK576	FB/EFI/PAIR/EGR/OC.	No	Changes in hardware between tests and insufficient number of data points.	1981 development.	NSA, p. 5.
119	HB194	FB/EFI/PAIR/EGR/OC.	No	Changes in calibration between tests	1981 development.	NSA, p. 7.
90.8	AK714	AIR/EGR/OC.	No	Calibrations changed between tests	1981 development.	NSA, P. 9.
90.8	AK618	AIR/EGR/OC.	No	Calibration changes between tests	1981 development.	NSA, P. 11.
90.8	AK715	AIR/EGR/OC.	No	Not a durability car	1981 development.	NSA, 13–14.
90.8	K110	AIR/EGR/OC.	No	Not a durability car	1981 development.	NSA, p. 16–17.
90.8	AW34	AIR/EGR/OC.	No	Not a durability car	1981 development.	NSA, p. 19. NSS[3], p. 36–37.
90.8	A454	AIR/EGR/OC.	No	Not a durability car	1981 development.	NSA, p. 21.
90.8	AK577	AIR/EGR/OC.	No	Not a durability car	1981 development.	NSA, p. 23.
146	BW235	EFI/EGR/3W	No	Not a durability car	1981 development.	NSA, p. 27.
146	B1804	EFI/EGR/3W	No	Not a durability car	1981 development.	NSA, p. 29.
119	B2085	FB/PAIR/EGR/OC.	No	Insufficient mileage accumulation	1981 development.	NSA, p. 31.
90.8	AK579	AIR/EGR/OC.	No	Insufficient number of data points	1981 development.	NSA, p. 33.
90.8	A612	AIR/EGR/OC.	Yes		1981 development.	NSA, p. 35. NSS, p. 55.
119	BK598	FB/PAIR/EGR/OC.	No	Insufficient number of data points	1980 development.	NSA, pp. 15–16.
168	F763	EFI/3W	No	Insufficient number of data points	1981 development.	NSA, pp. 19–20.
119	AK861	FB/EFI/PAIR/EGR/OC.	No	Insufficient number of data points	1981 development.	NSA, pp. 23–24.
90.8	AW25	AIR/EGR/OC.	No	Insufficient number of data points	1980 development.	NSA, pp. 26–27
85.2	A458	AIR/EGR/OC.	No	Insufficient number of data points	1978 development.	NSA, pp. 29–30.
119	AK363	EFE/PAIR/EGR/OC.	No	Changes in hardware between tests	1978 development.	NSS, pp. 31–32.
168	F503	EVE/PAIR/EGR/OC.	No	Changes in hardware between tests	1978 development.	NSS, p. 33–34.
168	BW220	ECCS/3W	No	Changes in hardware between tests	ECCS development.	NSS, p. 39–40.
119	BK579	FB/EFI/EGR/PAIR/OC.	No	Changes in hardware between tests	1980 development.	NSSS[4], pp. 16–17.

[1] NWA is used here as an abbreviation for reference 2.

[2] NSA is used here as an abbreviation for reference 15.

[3] NSS is used here as an abbreviation for reference 13.

[4] NSSS is used here as an abbreviation for reference 19.

Pass/Fail Analysis of Vehicles Using the 75 CID Engines

Nissan provided durability data that were acceptable for computer analysis on one vehicle. This was vehicle number A–883, and this was a 1980 model year California certification vehicle representing the Nissan family A12C. Car A–883 was equipped with an AIR/EGR/OC system which is Nissan's first choice system for vehicles using the 75 CID engine in model year 1981 [5 at 56]. The only emission hardware changes planned by Nissan for 1981 are the addition of an improved oxidation catalyst [5 at 56] and dual-walled exhaust pipes if needed [13 at section IV, p. 13]. Calibration modifications could also be incorporated for the choke, ignition timing, and AIR system [5 at 56]. Since Nissan claimed their catalyst descriptions to be confidential, the precise improvements incorporated into the oxidation catalyst cannot be discussed.

An emission control system consisting of FI or FBC/EGR/AIR/3W/OC is considered to be the prime emission control system for meeting 0.41 HC, 3.4 CO, 1.0 NOx by the EPA technical staff (the prime system being the one most capable of achieving 0.41 HC, 3.4 CO, 1.0 NOx). A system such as this was not tested by Nissan with vehicles using the 75 CID or any other engine. The technical staff believes that the cost of the prime system versus Nissan's first choice system (particularly for the vehicles with 75, 85 and 91 CID engines) was the reason that Nissan did not pursue the prime system [5 at 72–73].

The complete emission results of car A–883 are shown in table V–4.

Table V-4.—*Nissan California Durability Vehicle for the 1980 Model Year*

[Engine family A12C; vehicle A-883]

Miles	75 FTP results		
	HC	CO	NOx
4810.	0.249	2.88	0.95
9861.	0.169	2.13	0.88
15161.	0.189	2.49	0.84
15182.	0.237	2.92	0.80
19839.	0.191	2.36	0.85
24794.	0.225	1.45	0.84
30099.	0.233	2.01	0.87
30117.	0.213	1.45	0.81
34799.	0.231	1.69	0.85
40170.	0.214	1.36	1.01
44860.	0.251	1.55	0.85
44879.	0.218	1.74	0.82
50016.	0.235	1.69	0.85
4000.(CALC)	0.20548	2.66137	0.86946
50000.(CALC)	0.23252	1.35492	0.85725
Deterioration factor	1.132	0.509	0.986

On the basis of vehicle A–883, Nissan can certify vehicles using 75 CID engines family A12C as used in 1980 certification.

A predictive methodology is not necessary in this case as a vehicle has actually been run in certification using technology similar to that planned for use by Nissan in 1981. But as an illustrative example of the conservatism employed in the Monte Carlo, car A–883 (and a few others in similar situations) was entered into Monte Carlo. The vehicle was entered and run with no factors. The predicted probabilities of passing HC, CO, and NOx were 100, 100 and 77. The vehicle would have failed NOx by a small margin as a minimum value of 80% is required for each pollutant.

Pass/Fail Analysis of Vehicles Using the 85 and 91 Engines

The data from vehicles using the 85 and 91 CID engines were analyzed together as they have historically been in the same engine family in EPA certification.

Data from a total of six vehicles were entered into the Monte Carlo analysis. No cars presented by Nissan were rejected for any reason other than that they did not meet the minimum criteria for number of points or mileage accumulation.

Three of the six vehicles (AK749, AK0522, and YBU21) are actual certification vehicles. Vehicle A612 was a 1981 model year prototype (only one of two 1981 prototypes presented by Nissan which had 20,000 miles for more of durability). Vehicles A609 was a 1979 development vehicle and vehicle A555 was a 1980 development vehicle.

Actual certification results of the three certification durability vehicles are presented in table V–5.

The first choice Nissan system for achieving the 1981 emission standards of 0.41 HC, 3.4 CO, 1.0 NOx with vehicles using these engines is an AIR/EGR/OC system. Improved components in this emission control system for 1981 compared to the 1980 models using the same basic system are an improved oxidation catalyst and dual-walled exhaust pipes. The dual-walled pipes will only be used if needed. [5 at 56 and 13 at section IV, p. 13]. Calibration changes could include revisions to the choke calibration, spark timing, and AIR system calibration [5 at 56].

The Monte Carlo simulation predicted the probabilities of passing for these vehicles as shown in table V–6.

Table V-5.—*Results of Nissan Certification Vehicles*

	Vehicle AK 749 (80 certification family A14/15C)				Vehicle AK0522 (78 certification family A140C)				Vehicle YBU21 (80 certification family A14/15C)			
	Miles	HC	CO	NO$_x$	Miles	HC	CO	NO$_x$	Miles	HC	CO	NO$_x$
	4840.	0.196	2.05	0.99	5181.	0.270	2.00	1.04	5152.	0.289	3.95	0.89.
	9777.	0.282	3.52	0.93	9776.	0.320	2.50	1.02	9848.	0.265	4.27	0.83.
	15137.	0.257	3.26	0.88	15182.	0.250	2.30	1.20	15088.	0.265	3.84	0.80.
	15157.	0.261	2.96	0.80	15201.	0.240	2.30	0.95	15108.	0.279	3.17	0.78.
	19798.	0.288	3.88	0.89	19819.	0.260	2.10	1.10	19851.	0.293	3.38	0.82.
	25063.	0.219	2.26	1.00	25101.	0.220	2.10	1.03	25155.	0.286	3.19	0.83.
	29828.	0.220	3.16	0.89	30192.	0.230	2.80	1.12	29926.	0.312	4.07	0.91.
	29846.	0.220	1.97	0.94	30213.	0.230	2.10	1.05	29945.	0.310	4.00	0.80.
	35156.	0.295	2.94	0.89	35188.	0.210	2.60	1.10	35157.	0.277	3.56	0.90.
	39799.	0.265	2.72	0.90	40002.	0.250	3.60	1.29	40158.	0.339	4.50	0.75.
	44768.	0.305	3.65	0.99	45184.	0.220	3.10	1.03	45121.	0.307	2.96	0.90.
	44787.	0.248	2.55	0.85	45203.	0.250	2.60	1.03	45140.	0.279	3.09	0.82.
	50008.	0.271	3.21	0.92	50011.	0.260	2.50	0.85	50025.	0.302	2.90	0.89.
4000.(CALC)=		0.23730	2.86379	0.91505		0.26849	2.06299	1.08082		0.27471	3.96317	0.82385.
50000.(CALC)=		0.27300	2.99660	0.91127		0.22745	2.90922	1.04559		0.30870	3.28254	0.85464.
Deterioration factor=		1.150	1.046	0.996		0.847	1.410	0.967		1.124	0.828	1.037

Table V-6.——*Monte Carlo Results of Nissan Vehicles Using 85 and 91 CID Engines*

[Probability of pass]

VIN	Eng	Catalyst	HC	CO	NO$_x$	Comment
AK749	85	D	97	69	78	1980 Calif. cert vehicle.
AK0522	85	V	99	78	29	1978 Calif. cert vehicle.
YBU21	85	H	92	7	82	1980 Calif. cert vehicle.
A612	91	F	94	36	97	1981 developmental vehicle has improved catalyst.
A609	85	H	100	14	8	1979 developmental vehicle.
A555	91	D	100	0	54	1980 developmental vehicle
With factors for ignition time recalibration during cold start.						
AK749			100	98	79	
AK0522			100	99	32	
YBU21			96	89	82	
A612			97	81	97	
A609			100	61	9	
A555			100	51	56	

Since there is already a Nissan engine family certified to the 1981 emission standards (as shown by vehicle AK749), the Monte Carlo simulation was not necessary in this case. However, with the factor for revised ignition timing during cold start the Monte Carlo confirms Nissan's ability to certify in 1981 (on the basis of vehicle A612 using the improved catalyst). Vehicle A612 is the only vehicle of the six designed specifically for 1981 Federal emission standards. None of the other five vehicles used the improved catalyst.

Pass/Fail Analysis of Vehicles Using the 119 CID Engines

Four different emission control systems have been developed by Nissan for vehicles using the 119 CID engines. These emission control systems and individual vehicles utilizing these emission control systems are shown in table V–7. Again, no vehicles submitted by Nissan were rejected from the analysis.

Table V-7.—*Nissan Durability Vehicles Using 119 CID Engines*

VIN	Emission control system	Catalyst**	Comments
BK649	FB*/PAIR/EGR/OC	P	80 Calif. cert vehicle.
B1968	FB/PAIR/EGR/OC	Q	80 Calif. development vehicle.
8D-991	FB/PAIR/EGR/OC	A	80 Calif. development vehicle.
8D-992	FB/PAIR/EGR/OC	A	80 Calif. development vehicle.
AK690	FB/EFI/PAIR/EGR/OC	A	80 Calif. cert vehicle.
BK584	FB/EFI/PAIR/EGR/OC	A	80 Calif. development vehicle.
YD021	FB/EFI/EGR/3W	S	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.
YD020	FB/FBC/EGR/3W	K	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.

*FB means fast burn.

**Different catalysts generally indicate that the vehicles would be in different engine families in certification..

Of the four emission control systems in table V–7, the systems of FB/PAIR/EGR/OC (carbureted) and FB/EFI/PAIR/EGR/OC are planned for use by Nissan in 1981 to meet 0.41 HC, 3.4 CO, 1.0 NO$_x$. For the carbureted system, Nissan has the additional options of using an improved oxidation catalyst, dual-walled exhaust pipes, and a new, proprietary device in 1981 [5 at 55 to 56 and 13 at section IV, p. 13]. Calibration modifications could include a leaner choke and a leaner "engine air/fuel" ratio [5 at 55 to 56]

According to Nissan, the emission control system on vehicle YD020 cannot be used in model year 1981 due to the high CO emissions from the system [5 at 70 to 71]; however, all hardware will be available to build vehicles like car YD021 in 1981 [5 at 70]. Nissan expressed concern about the durability of the system used on car YD021, particularly for model year 1981 use. This concern is not shared by the EPA technical staff as Nissan is gaining production experience with the fuel injection system (open loop version) in 1980 with family Z20FC (119 CID) and production experience with oxygen sensors, closed loop electronics and 3-way catalysts in 1980 with family L24/28C (168 CID).

No emission control systems incorporating prime technology (3W+OC) have been developed for vehicles using the 119 CID engines.

The complete emission results of the two 1980 California certification vehicles are shown in table V–8. Vehicle AK690 achieved the 1981 Federal emission standards of 0.41 HC, 3.4 CO, 1.0 NOx. Vehicle YD–021 also achieved emission levels well below the 0.41 HC, 3.4 CO, 1.0 NOx standards. The complete emission results from this vehicle are shown in table V–8.

Table V-8.—*1980 California Certification Vehicles Using 119 CID Engines*

	Family Z20EC VIN AK690				Family Z20SC VIN BK649			
	Miles	HC	CO	NO_x	Miles	HC	CO	NO_x
	4841.	0.261	1.88	0.96	4811.	0.278	6.53	.052
	9839.	0.261	1.58	0.81	10079.	0.328	8.03	0.56
	15184.	0.314	1.86	1.00	15160.	0.224	6.48	0.50
	15203.	0.325	1.81	0.99	15178.	0.260	6.16	0.57
	20151.	0.339	1.74	1.02	20147.	0.298	4.01	0.62
	24823.	0.297	1.84	0.92	24934.	0.283	6.39	0.64
	30155.	0.297	1.71	0.93	29875.	0.267	6.34	0.75
	30172.	0.305	1.87	0.82	29893.	0.301	5.53	0.60
	34941.	0.291	1.78	0.81	34770.	0.313	6.71	0.56
	40149.	0.292	1.75	0.83	40158.	0.312	5.98	0.60
	44836.	0.321	1.75	0.85	44767.	0.272	6.43	0.51
	44855.	0.297	1.69	0.89	44785.	0.340	6.93	0.60
	50013.	0.342	1.86	0.85	50018.	0.329	6.08	0.50
4000. (CALC)=		0.28524	1.78370	0.96422	0.56594	0.26792	6.40847	
5000. (CALC)=		0.31959	1.77370	0.83865	0.57665	0.31531	6.15680	
Deterioration factor=		1.120	0.994	0.870	1.019	1.177	0.961	

Table V-9.—*Emission Results of Car YD-021 Using the 119 CID Engine With EFI/EGR/3W*

[Datsun 510 at 2750 IW]

	1975 FTP				
Miles	HC	CO	NO_x	MPGu	Maintenance
0	0.13	1.26	0.13	25.9	
5,000	0.16	1.82	0.15	25.5	
10,000	0.16	2.08	0.21	25.4	
15,000	0.24	1.79	0.29	25.7	Replaced engine oil and oil filter.
20,000	0.17	1.74	0.34	26.2	
25,000	0.19	2.18	0.31	26.1	
30,000	0.17	1.72	0.37	26.4	Replaced engine oil, oil filter and spark plug.
30,000	0.24	2.54	0.33	25.8	After maintenance
35,000	0.20	2.10	0.39	26.3	
40,000	0.24	2.72	0.47	26.2	
45,000	0.21	2.39	0.48	26.5	Replaced engine oil and oil filter.
50,000	0.23	2.43	0.46	26.7	
4,000 (CALC)	0.17	1.75	0.18		
50,000 (CALC)	0.23	2.50	0.50		
Deterioration factor=	1.3569	1.4225	2.7855		

All eight vehicles were run through the Monte Carlo simulation. The results are presented in table V–10.

Table V-10.—*Results of the Monte Carlo Analysis for Vehicles Using 119 CID Engines*

VIN	Emission control system	Probability of pass		
		HC	CO	NO_x
	Without Factors			
BK 649	FB/PAIR/EGR/OC	92	0	99
B1968	FB/PAIR/EGR/OC	88	92	14
8D-991	FB/PAIR/EGR/OC	61	51	96
8D-992	FB/PAIR/EGR/OC	94	59	96
AK 690	FB/EFI/PAIR/EGR/OC	90	100	63
BK 584	FB/EFI/PAIR/EGR/OC	90	0	31
YD021	FB/EFI/EGR/3W	100	92	100
YD020	FB/FBC/EGR/3W	100	1	100
	With Factors for Improved Oxidation Catalyst and Dual-Walled Exhaust Pipe			
BK649		97	0	98
B1968		97	100	10
8D-991		90	87	96
8D-992		99	98	95

Based on completed certification testing, Nissan can sell vehicles using the 119 CID engine and the FB/EFI/PAIR/EGR/OC emission control system in 1981.

Based on Monte Carlo anaylsis, Nissan could also certify vehicles using the 119 CID engine and either the FB/EFI/EGR/3W emission control system or FB/PAIR/EGR/OC system as represented by vehicles 8D–991 or 8D–992 (using catalyst A and a dual-walled exhaust pipe).

Pass/Fail Analysis of Vehicles Using the 146 and 168 CID Engines

Vehicles using these two engines were analyzed together as they also have historically been certified as a single engine family in EPA certification. All of the vehicles discussed in this section actually used the 168 CID engine.

No vehicles submitted by Nissan were rejected from this analysis for any reason except that they did not either accumulate sufficient mileage (20,000 miles minimum without a substantial change in calibration or hardware) or have a sufficient number of data points to be included in the deterioration factor calculation (4 points as a minimum).

Two basic emission control systems could be utilized by Nissan in 1981 for vehicles using these engines. Those systems are EFI/3W and EFI/EGR/3W [5 at 57 and 5 at 81]. No systems using a 3W + OC system were tested on durability vehicles. Also, no start-up AIR systems were tested on any vehicles. One vehicle (F671) was run with EFI/EGR/3W/3WSC, but results were not encouraging with the addition of the start catalyst and Nissan has no plans to market such a vehicle.

Additional hardware which could be utilized by Nissan for vehicles using these engines in 1981 includes an improved 3-way catalyst [5 at 81].

The vehicles entered into the Monte Carlo simulation are shown in table V–11. Again different catalyst codes would indicate that the vehicles would be in different certification engine families. Only one vehicle (car F671) appeared to be designed for the 1981 emission standards. The results of the Monte Carlo analysis are shown in table V–12.

Table V-11.—*Nissan Vehicles Using 168 CID Engines That Were Entered Into Monte Carlo Analysis*

VIN	Engine	Emission control system	Catalyst Code	Comments
F614	168	EFI/EGR/3W	K	80 Calif. development vehicle.
F675	168	EFI/EGR/3W	K	80 Calif. development vehicle.
F836	168	EFI/3W	K	80 Calif. cert. vehicle.
8D-645CA*	168	EFI/3W	W	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.
8D-645CB*	168	EFI/3W	L	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.
8D-645CC*	168	EFI/3W	W	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.
F615	168	EFI/3W	K	Targeted for 0.41 HC, 3.4 CO, 0.4 NO$_x$.
F671	168	EFI/EGR/3W/3WSC.	θ+X	Experimental vehicle for 1981.

*These are actually all vehicle 8D-645C. The A and C cases use catalyst W, but are different durability runs (C was actually run first). Case B was run simultaneously with case A using a catalyst designated at catalyst L.

Table V-12.—*Monte Carlo Analysis of Nissan Vehicles Using 168 CID Engines*

VIN	Emission control system	Catalyst	Probability of pass		
			HC	CO	NO$_x$
	No Factors				
F614	EFI/EGR/3W	K	87	43	99
F675	EFI/EGR/3W	K	85	94	100
F836	EFI/3W	K	84	0	100
8D-645CA	EFI/3W	W	80	48	100
8D-645CB	EFI/3W	L	88	29	100
8D-645CC	EFI/3W	W	80	50	100
F615	EFI/3W	K	94	82	100
F671	EFI/EGR/3W/3WSC	θ+X	11	17	100
	With Factors for Start-up Air Injection				
F614			97	78	100
F675			97	100	100
F836			97	13	100
8D-645CA			96	81	100
8D-645CB			100	75	100
8D-645CC			96	82	100
F615			99	99	100

For those vehicles using EFI/EGR/3W (catalyst K) emission control systems, one passes and one fails. Since both use identical emission control systems a two car analysis was run to determine if this system could certify. The results of the two car analysis are as follows:

	Probability of pass
HC	80
CO	66
NO_x	99

A similar two car analysis could have been run using other pairs of identical vehicles, such as F836 and F615, but the low CO probability of pass for F836 indicates that the pair would fail also.

On the basis of the two car analysis of vehicles F614 and F675, this family is projected to fail without factors.

With the use of factors for the addition of warm-up air injection, the ability of Nissan to certify was enhanced. A two car analysis of cars F614 and F675 indicate that the emission control system of EFI/EGR/3W (catalyst K) with warm-up air injection can certify. The respective probabilities of pass are 97 for HC, 90 for CO, and 100 for NOx. A two car analysis with the emission control system of EFI/3W (catalyst W) and warm-up air injection was not needed as vehicles 8D/645CA and 8D-645CC both pass in the single car analysis.

On the basis of the success discussed above, the vehicles using 168 CID engines are considered to pass with the factors for the addition of warm-up air injection.

Pass/Fail Analysis of Vehicles Using Engines in Families A and B

No data were presented by Nissan that were acceptable for entry into the EPA model. Thus, these families are considered as "no data" families. It is clear, based on Nissan's projected sales, that the basic market demand for Nissan vehicles could be met without the use of these two engine families.

Renault

Renault applied for a waiver of the 3.4 gm/mile CO standard only for their 85 cubic inch displacement LeCar engine. Table V–13 lists the vehicles for which Renault submitted data in support of their waiver request. The list only includes durability data vehicles with engines for which a waiver was requested.

Table V–13.—*Renault Durability Vehicles*

	VIN	Catalyst	Entered in Monte Carlo?	If not entered, why?	References
Engine (CID):					
85	TP–28	PTX 5302.	Yes		4 at V/I.
85	TP–29	TWC–16.	Yes		4 at V/I.
85	573	TWC–16.	Yes		17 at V/A p. 2; 45 at 2.
85	540	3W+OC.	No	Insufficient number of data points.	18 at 2.2; 43 at 4.

Pass/Fail Analysis for the Renault 85 CID Engine

The 85 CID engine family is projected to pass with hardware improvement factors for a clean up oxidation catalyst with a switched AIR system. This family is projected to fail without hardware improvement factors. This analysis is based on the results of vehicles TP–29 and 573 both of which pass with the aforementioned improvements and fail without improvements.

Renault submitted durability data on four vehicles. Vehicles TP–79 and 573 only had a single three-way catalyst system, whereas vehicle 540 had the 3-way plus oxidation catalyst system (with switched air injection and EGR) which Renault has selected as their first choice emission control system to meet the 1981–1982 standards.

The EPA technical staff decided to apply factors to the three-way only vehicles, rather than the three-way plus oxidation catalyst vehicle (540) for several reasons. First, vehicle 540 had insufficient data for the Monte Carlo analysis. Also, it was apparent from the data which was submitted that vehicle 540 had higher emissions than vehicles TP–29 and 573 had with the improvement factors for a clean up oxidation catalyst with a switched AIR system.

If a manufacturer does not submit durability data for a prime* emission control system, the technical staff attempts to simulate a prime system with hardware improvement factors. Where data are submitted for a prime system, there is no need to simulate, and factors need not be applied. Although Renault identified a vehicle (540) which includes the components of a prime emission control system, in the EPA technical staff's judgment, its configuration is not optimized in that the oxidation catalyst is further downstream than would be optimum for HC & CO control. In order to simulate a prime system, the technical staff would have to apply a factor for catalyst location. Since such a factor has not been developed and the vehicle could not be entered into the analysis, EPA applied the factors for a clean up oxidation catalyst with a switched AIR system to vehicles TI–29 and 573. This allowed EPA to simulate a prime emission control system.

Renault stated that the conversion efficiency of the oxidation catalyst in their first choice system was poor because it had to be located too far from the engine due to space constraints [4 at V/4]. In a response to an EPA request for substantiation of their space constraints, Renault sent a drawing [43 at 3] showing their present oxidation catalyst location, but not showing the area in the vicinity of the three-way catalyst. Reviewing a prior drawing [44 at 5.3] submitted to support their contention that three-way catalyst could not be increased in volume, it appears possible that an oxidation catalyst could be mounted vertically in the engine compartment. Although the drawing showed catalyst interference with the tire for a vertically mounted catalyst, it showed no constraints in moving the catalyst such that it would not interfere with the tire or consideration for the use of an oval shaped catalyst. Because the information submitted by Renault did not substantiate that the oxidation catalyst couldn't be moved into a position where it could operate more efficiently, the technical staff judged that it would be valid to apply improvement factors to vehicles TP–29 and 573. Based on the results of these vehicles, the 85 CID engine family is projected to pass with hardware improvement factors for a clean up oxidation catalyst with a switched AIR system.

Table V–14 lists the Monte Carlo results for the durability vehicles submitted by Renault.

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*A prime system is considered by EPA to be FBC/EGR/3W/OC switched AIR used in an optimized configuration.

Table V-14.—*Monte Carlo Results of Renault Durability Results*

VIN	Emission control system	Probability of pass			Comments
		HC	CO	NO_x	
TP-28	AIR/OC/EGR	97	100	4	No factors.
TP-29	FBC/3W/EGR	98	0	100	No factors.
TP-29-2	FBC/3W/EGR	100	96	100	Factors for a clean up oxidation catalyst with a switched AIR system.
573	FBC/3W/EGR	88	0	100	No factors.
573-2	FBC/3W/EGR	100	98	99	Factors for a clean up oxidation catalyst with a switched AIR system.

Toyo Kogyo

Toyo Kogyo has requested a waiver for vehicles powered by three engines. These are the 70 CID rotary engine, the 91 CID conventional engine and the 120 CID conventional engine. TK has two distinct sets of technology planned for possible use in 1981. One set would be used for attempting to meet a 3.4 CO standard and the other would be used at 7.0 CO. Both sets of technology used open loop carburetion, air injection, 3-way catalysts and oxidation catalysts. The primary differences between these two sets of technology are in the details of the system operation and system calibration. Details of the differences were claimed to be confidential by TK.

The vehicles presented by TK in their waiver application are summarized in table V-15. A large number of development vehicles were run; however, a much smaller number of durability vehicles were run.

TK did indicate that there were currently problems with their open loop emission control systems with high catalyst bed temperatures (see system C-1 in reference 30 on pages II-3, II-4 and II-5). Also, these particular systems are the first choice systems of TK for meeting either a 0.41 HC, 3.4 CO, 1.0 NOx standard or a 0.41 HC, 7.0 CO, 1.0 NOx standard in 1981 with their vehicles using 91 and 120 CID engines (see reference 40 at pages 3 to 5). It is assumed by the EPA technical staff that these systems will not be marketed by TK without resolution of this problem due to potential problems of consumer safety.

Technological solutions (temperature or speed/load controlled AIR systems) for the catalyst overtemperature problem have existed for a number of years and there would be no excuse for marketing vehicles with this problem. The move to close loop emission control systems in place of the open loop systems is expected to improve the situation for TK. At the same time their catalyst deterioration and CO control problems are expected to improve.

Table V-15.—*Vehicles in Toyo Kogyo Wavier Application*

Engine	VIN	Emission control system [2]	Entered in Monte Carlo	If not entered in Monte Carlo—Why?	Comment	Reference
86.4	(UC) No VINs given		No	No waiver requested for this engine	1979 GLC	TWA,[1] sec. IV, p 44.
120.2	(MA) No VINs given		No	Insufficient number of data points	1980 626	TWA, sec. IV, p 45.
	1		No	Insufficient number of data points	1978 GLC	TWA, sec. IV, p 98.
	2		No	Insufficient number of data points	1978 RX-3 sp	TWA, sec. IV, p 98.
	3		No	Insufficient number of data points	1979 626	TWA, sec. IV, p 98.
	4		No	Insufficient number of data points	1979 GLC	TWA, sec. IV, p 98.
35X2	RE-F-1	AIR/EGR/OC	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-2	AIR/EGR/OC	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-3	AIR/EGR/OC	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-4	AIR/EGR/OC	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-5	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-6	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-7	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-8	AIR/EGR/TR	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-9	AIR/EGR/TR	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-10	AIR/EGR/TR	No	Insufficient number of data points		TWA, sec. V, p 120.
35X2	RE-F-11	AIR/EGR/TR	No	Insufficient number of data points		TWA, sec V, p 120.
35X2	RE-F-12	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 120.
35X2	RE-F-13	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 120.
35X2	RE-F-14	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 120.
35X2	RE-F-15	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 120.

Table V-15.—*Vehicles in Toyo Kogyo Wavier Application*—Continued

Engine	VIN	Emission control system [2]	Entered in Monte Carlo	If not entered in Monte Carlo—Why?	Comment	Reference
35X2	RE-F-16	AIR/3W/OC	Yes			TWA, sec V, p 121.
35X2	RE-F-17	AIR/3W/OC	Yes			TWA, sec V, p 121.
35X2	RE-F-18	AIR/3W/OC	Yes			TWA, sec V, p 121–122, TSS, p 122.
35X2	RE-F-19	AIR/3W/OC	Yes			TWA, sec V, p 122, TSS, p 122.
35X2	RE-F-20	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 122, TSS, p 122.
35X2	RE-F-21	AIR/3W/OC	No	Insufficient number of data points		TWA, sec V, p 122, TSS, p 122.
35X2	RE-F-22	AIR/3W/OC	Yes			TWA, sec V, p 123, TSS, p 123.
35X2	RE-F-23	FBC/AIR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 123, TSS, p 123.
35X2	RE-F-24	FBC/AIR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 123, TSS, p 123.
35X2	RE-F-25	FBC/AIR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 123, TSS, p 123.
35X2	RE-F-26	EFI/AIR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 123, TSS, p 123.
35X2	RE-F-27	EFI/AIR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 123, TSS, p 123.
86.4	CE-F-1	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-2	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-3	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-4	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-5	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-6	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-7	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
86.4	CE-F-8	AIR/EGR/3W	No	No waiver requested for this engine		TWA, sec V, p 124.
120.2	CE-F-9	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
120.2	CE-F-10	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
120.2	CE-F-11	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
120.2	CE-F-12	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
120.2	CE-F-13	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
120.2	CE-F-14	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 124.
90.9	CE-F-15	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
90.9	CE-F-16	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
90.9	CE-F-17	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
90.9	CE-F-18	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
90.9	CE-F-19	AIR/EGR/3W	Yes			TWA, sec V, p 125.
90.9	CE-F-20	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
90.9	CE-F-21	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
120.2	CE-F-22	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
120.2	CE-F-23	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
120.2	CE-F-24	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 125.
120.2	CE-F-25	AIR/EGR/3W	Yes			TWA, sec V, p 125.
120.2	CE-F-26	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 126.
120.2	CE-F-27	AIR/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 126.
90.9	CE-F-28	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 126.
90.9	CE-F-29	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 126.

Table V-15.—*Vehicles in Toyo Kogyo Wavier Application*—Continued

Engine	VIN	Emission control system [2]	Entered in Monte Carlo	If not entered in Monte Carlo—Why?	Comment	Reference
90.9	CE-F-30	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 126.
90.9	CE-F-31	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 126.
90.9	CE-F-32	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 127, TSS, p 130a.
90.9	CE-F-33	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 127.
90.9	CE-F-34	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 127.
90.9	CE-F-35	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 127.
90.9	CE-F-36	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 127-128, TSS, p 130a.
120.2	CE-F-37	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 128, TSS, p 130.
120.2	CE-F-38	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 128, TSS, p 130.
120.2	CE-F-39	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 128, TSS, p 130.
120.2	CE-F-40	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 128.
120.2	CE-F-41	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 128-129, TSS, p 130a.
120.2	CE-F-42	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 128, TSS, p 130a.
120.2	CE-F-43	AIR/EGR/3W/OC.	No	Insufficient number of data points		TWA, sec V, p 128.
90.9	CE-F-44	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 130, TSS, p 130.
120.2	CE-F-45	AIR/EGR/3W/OC.	Yes			TWA, sec V, p 130, TSS, p 130.
90.9	ADV-F-1	FBC/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
90.9	ADV-F-2	FBC/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
90.9	ADV-F-3	FBC/EGR/3W	Yes			TWA, sec V, p 131,TWS,[3] p III-13.
120.2	ADV-F-4	FBC/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-5	FBC/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-6	FBC/EGR/3W	Yes	Insufficient number of data points		TWA, sec V, p 131, TWS, p III-13.
120.2	ADV-F-7	SPFI/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-8	SPFI/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-9	EFI/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-10	EFI/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
120.2	ADV-F-11	EFI/EGR/3W	No	Insufficient number of data points		TWA, sec V, p 131.
90.9	CE-F-46	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-47	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-48	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-49	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-50	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-51	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130b.
90.9	CE-F-52	AIR/EGR/3W/OC.	Yes			TSS, p 130b.
90.9	CE-F-53	AIR/EGR/3W/OC.	Yes			TSS, p 130b-130c.
120.2	CE-F-54	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130c.
120.2	CE-F-55	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130c.

Table V-15.—*Vehicles in Toyo Kogyo Wavier Application*—Continued

Engine	VIN	Emission control system ²	Entered in Monte Carlo	If not entered in Monte Carlo—Why?	Comment	Reference
120.2	CE-F-56	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130c.
120.2	CE-F-57	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130c.
120.2	CE-F-58	AIR/EGR/3W/OC.	No	Insufficient number of data points		TSS, p 130c.
120.2	CE-F-59	AIR/EGR/3W/OC:	No	Insufficient number of data points		TSS, p 130c.
120.2	CE-F-60	AIR/EGR/3W/OC.	Yes			TSS, p 130c.
120.2	CE-F-61	AIR/EGR/3W/OC.	Yes			TSS, p 130d.
35X2	RE-F-28	FBC/EGR/AIR/3W/OC.	No	Insufficient number of data points		TWS, p III-13

[1] TWA is used here as an abbreviation for reference 1.

[2] TK was not always clear about the use of AIR or PAIR, AIR has been assumed in all questionable cases.

[3] TWS is used here as an abbreviation for reference 30.

Pass/Fail Analysis of Vehicles Using the 70 CID Rotary Engine

In their effort to achieve the 1981 emission standards of 0.41 HC, 3.4 CO, 1.0 NOx, Toyo Kogyo ran a total of six durability vehicles which could be entered into the EPA Monte Carlo Analysis. Five of those vehilces (RE-F-16, RE-F-17, RE-F-18, RE-F-19 and RE-F-22) were prototypes equipped with open loop carburetor/AIR/3W/OC/3WSC systems. These vehicles were essentially identical, according to the vehicle and emission control system descriptions provided by TK. The last vehicle (ODREP-2) was a certification vehicle for California in 1980 using exhaust gas recirculation, air injection and a thermal reactor. Vehicles RE-F-16 and RE-F-17 and RE-F-22 were calibrated specifically for the 1981 Federal emission standards. The other two cars were targeted for the 1981 California emission standards [1 at 36 to 37 and 34 at Status of Present Emission Level].

None of the vehicles submitted by TK were rejected from the Monte Carlo analysis. Vehicle ODREP-2 was not entered in the Monte Carlo as a predictive methodology is not needed when an actual certification vehicle is being considered.

The first choice system of Toyo Kogyo for use in the 1981 model year is the same as that used on the five identical vehicles discussed above [5 at 11]. Improvements which could be incorporated for the 1981 to 1982 model years include recalibration of the ignition timing and increased catalyst noble metal loadings, according to TK [30 at II-2]. This system is not considered to be a prime system by the EPA technical staff because the system is open loop and there is no indication in the TK waiver application that EGR has been optimized with the 3W + OC emission system. These two factors are highly probable causes of high CO emissions from TK vehicles using rotary engines.

The lack of feedback control results in air-fuel ratios below stoichiometry to provide a reducing atmosphere in the 3-way catalyst. If this does not provide sufficient NO_x control, the air-fuel ratio is probably even further reduced due to the absence of EGR. Both of these reductions in air-fuel ratio would tend to increase engine-out and tailpipe CO emissions.

The Monte Carlo results of the five prototype vehicles are shown in table V-16. All five vehicles failed. The EPA technical staff was unable to generate factors to account for the previously mentioned deficiencies in the emission control system for the rotary engine.

Table V-16.—*Monte Carlo Results of TK Vehicles Using Rotary Engines*

VIN	Emission control system	Probability of pass HC	Probability of pass CO	Probability of pass NO_x
Without factors (Catalysts D, D and C)				
RE-F-16	Open loop/AIR/3W/OC/3WSC	63	97	22
RE-F-17	Open loop/AIR/3W/OC/3WSC	63	99	7
RE-F-18	Open loop/AIR/3W/OC/3WSC	97	0	100
RE-F-19	Open loop/AIR/3W/OC/3WSC	97	0	100
RE-F-22	Open loop/AIR/3W/OC/3WSC	87	48	96

The final vehicle (ODREP-2) utilized in the EPA analysis was the 1980 certification vehicle for California. This vehicle used a thermal reactor, EGR and air injection system. The complete emission results of this vehicle are shown in table V-17.

On the basis of the certification engine family OREP, vehicles using 70 CID rotary engines are projected to pass the 0.41 HC, 3.4 CO, 1.0 NOx emission standards. While this engine family utilizes an emission control system which is not the first choice system of TK, the system is already in production so lead time and driveability should not present insoluble problems for TK.

Table V-17.—*1980 Certification Results of Vehicle ODREP-2*

[Engine family OREP]

Miles	75 FTP HC	75 FTP CO	75 FTP NOx
5054	0.361	3.30	0.69
10102	0.350	3.19	0.68
14846	0.347	3.24	0.68
20025	0.358	3.37	0.67
24958	0.322	3.36	0.68
30104	0.318	3.07	0.65
30122	0.326	3.00	0.67
34884	0.309	2.41	0.64
40048	0.342	3.28	0.62
44932	0.351	3.36	0.67
49939	0.332	3.09	0.68
4000(CALC)	0.350	3.26	0.683
50000(CALC)	0.326	3.05	0.651
Deterioration factor	0.930	0.935	0.953

Pass/Fail Analysis of Vehicles Using 91 CID Conventional Engines

Data were submitted by TK for a total of seven durability vehicles. These were all prototype vehicles as no vehicles have been previously certified by Toyo Kogyo using the 91 CID engine. No vehicles submitted by TK were rejected from the Monte Carlo analysis except for reasons of insufficient durability mileage accumulation with a single emission control system or an insufficient number of test points. The seven vehicles in the analysis are shown in table V–18.

All the 3-way catalysts on the vehicles were located under the hood except the catalyst on car ADV–F–3 which was placed under the floor. Also all the vehicles were equipped with open loop carburetion except vehicle ADV–F–3 which had a feedback carburetor.

The first choice TK emission control system for model year 1981 is the open loop AIR/EGR/3W/OC system [5 at 12]. TK indicated that recalibrations of the emission control system and refinements in the catalyst protection system could be incorporated for the 1981 and 1982 model years [30 at II–3]. this is not considered to be a prime system by the EPA technical staff as the need for overly rich air-fuel mixtures to maintain reducing conditions in the 3-way catalyst results in excessive CO emissions.

Table V–18.—*TK Vehicles (Using 91 CID Engines) Entered Into the Monte Carlo Analysis*

VIN	Emission control system	Comment
CE–F–19	AIR/EGR/3W [1]	Open loop, catalyst functions as oxidation catalyst.
CE–F–32	AIR/EGR/3W/OC	Open loop.
CE–F–36	AIR/EGR/3W/OC	Open loop.
CE–F–44	AIR/EGR/3W/OC	Open loop, reduced secondary AIR at high speed and load.[2]
CE–F–52	AIR/EGR/3W/OC	Open loop, overtemperature protection device for rear catalyst.[2]
CE–F–53	AIR/EGR/3W/OC	Open loop, overtemperature protection device for rear catalyst.[2]
ADV–F–3	FBC/EGR/3W	Closed loop.

[1] This was called a 3-way catalyst by Toyo Kogyo, but it functions primarily as an oxidation catalyst.

[2] [34 at Status of Present Emission Level.]

Table V–18.—*TK Vehicles (Using 91 CID Engines) Entered Into the Monte Carlo Analysis*

VIN	Emission control system	Comment
CE–F–19	AIR/EGR/3W [1]	Open loop, catalyst functions as oxidation catalyst.
CE–F–32	AIR/EGR/3W/OC	Open loop.

Table V–18.—*TK Vehicles (Using 91 CID Engines) Entered Into the Monte Carlo Analysis*—Continued

VIN	Emission control system	Comment
CE–F–36	AIR/EGR/3W/OC	Open loop.
CE–F–44	AIR/EGR/3W/OC	Open loop, reduced secondary AIR at high speed and load.[2]
CE–F–52	AIR/EGR/3W/OC	Open loop, protection device for rear catalyst.[2]
CE–F–53	AIR/EGR/3W/OC	Open loop, overtemperature device for rear catalyst.[2]
ADV–F–3	FBC/EGR/3W	Closed loop.

[1] This was called a 3-way catalyst by Toyo Kogyo, but it functions primarily as an oxidation catalyst.

[2] [35 at Status of Present Emission Level.]

As shown in table V–19, the vehicle using the AIR/EGR/3W system failed HC and CO badly. This system is no longer under development by TK [1 at 39]. The five vehicles using the AIR/EGR/3W/OC all failed CO badly. The vehicle using the FBC/EGR/3W system failed CO, but was very close to passing (75% probability of passing the 3.4 CO standard—80% is needed).

Factors for hardware improvements were also applied to vehicle ADV–F–3. The additional hardware being simulated was a clean-up oxidation catalyst and switched air injection (to simulate a prime emission control system). The vehicle easily passed the emission standards of 0.41 HC, 3.4 CO, 1.0 NOx in this case. The very high probabilities of success with these factors indicate that TK may be able to pass using an emission control system that is less costly than the prime system which was analyzed.

This last simulation with vehicle ADV–F–3 has relevance for only the 1982 model year as TK provided adequate evidence [30 at section III] that they will not be able to build vehicles with feedback carburetion for the 1981 model year. Thus, vehicles using the 91 CID engines are projected to fail the 0.41 HC, 3.4 CO, 1.0 NOx standard in 1981. In 1982 they are projected to be able to pass using the FBC/EGR/AIR/3W/OC emission control system.

Table V–19.—*Probabilities of Passing the 0.41 HC, 3.4 CO, 1.0 NO$_x$ Standards for Vehicles Using 91 CID Engines*

VIN	*Emission control system*	Probability of pass		
		HC	CO	NO_x
	Without factors			
CE–F–19	AIR/EGR/3W* (catalyst A)	0	0	93.
CE–F–32	AIR/EGR/3W/OC (catalyst A and A)	74	11	100
CE–F–36	AIR/EGR/3W/OC (catalyst A and A)	68	0	100
CE–F–44	AIR/EGR/3W/OC (catalyst A and A)	79	2	100
CE–F–52	AIR/EGR/3W/OC (catalyst A and A)	99	29	100
CE–F–53	AIR/EGR/3W/OC (catalyst A and A)	84	29	100
ADV–F–3	FBC//EGR/3W (catalyst A)	100	75	100.
	With factors for the addition of AIR injection and a clean-up oxidation catalyst.			
ADV–F–3		100	100	100

*TK called this catalyst a 3-way catalyst even though it functions as an oxidation catalyst under most operating conditions.

Pass/Fail Analysis of Vehicles Using 120 CID Conventional Engines

A total of eight vehicles using the 120 CID engine were analyzed. Those vehicles are shown in table V–20. Again no vehicles that were submitted by TK were rejected from the analysis for any reason except failure to meet the minimum entry criteria.

The 3-way catalyst location was underhood on cars CE–F–25, ODMAP–1, CE–F–21, CE–F–42, CE–F–45, CE–F–60, and CE–F–61 and was underfloor on ADV–F–6. Those catalysts called "catalyst B" in table V–21 actually include catalysts that would be in more than one certification engine family; however, they could not be sorted due to the limitations of the information provided by TK.

TK's first choice system for use in 1981 to meet the 3.4 CO standard is the open loop AIR/EGR/3W/OC system [5 at 12]. Improvements which may be incorporated for the 1981 and 1982 model years include recalibrations and refinements to the catalyst overtemperature protection system [30 at II–5]. As discussed for the vehicles using 91 CID engines, this is not considered to be a prime emission control system by the EPA technical staff.

Table V-20—*TK Vehicles Utilizing 120 CID Engines That Were Entered Into the Monte Carlo Analysis*

VIN	Emission control system	Comment
CE-F-25	AIR/EGR/3W [1]	Open loop.
ODMAP-1	AIR/EGR/3W [1]	Open loop, 1980 California certification vehicle.
CE-F-41	AIR/EGR/3W/OC	Open loop.
CE-F-42	AIR/EGR/3W/OC	Open loop.
CE-F-45	AIR/EGR/3W/OC	Open loop,over temperature protection device for rear catalyst.[2]
CE-F-60	AIR/EGR/3W/OC	Open loop,over temperature protection device for rear catalyst.[2]
CE-F-61	AIR/EGR/3W/OC	Open loop, reduced secondary AIR at high speed/load.[2]
ADV-F-6	FBC/EGR/3W	Closed loop.

[1] These were called 3-way catalysts by TK, but they function primarily as oxidation catalysts.

[2] [34 at Status of Present Emission Level.]

When analyzed in the Monte Carlo analysis in the as received condition, all the TK vehicles failed CO as shown in table V-21. The more recent vehicles (CE-F-60 and CE-F-61); however, did show much improvement capability at 3.4 CO.

Hardware improvement factors were applied to vehicle ADV-F-6 for the addition of a clean-up oxidation catalyst and switched air injection. With the improved emission control system, car ADV-F-6 was projected to easily pass the 1981 Federal emission standard of 0.41 HC, 3.4 CO, 1.0 NO_x.

Due to the inability of TK to provide feedback control of the air-fuel metering system in 1981 for vehicles using 120 CID engines (as with all other TK vehicles for 1981), these vehicles are projected to fail the 3.4 CO emission standard in 1981, and the same vehicles are projected to pass the 0.41 HC, 3.4 CO, 1.0 NO_x standard in 1982 when feedback carburetion becomes available.

Table V-21.—*Monte Carlo Results of Toyo Kogyo Vehicles Using 120 CID Engines*

VIN	Emission control systems	Probability of pass HC	Probability of pass CO	Probability of pass NO_x
Without Factors				
CE-F-25	AIR/EGR/3W *(catalyst A)	0	0	53
ODMAP-1	AIR/EGR/3W *(catalyst A)	96	25	93
CE-F-41	AIR/EGR/3W/OC (catalysts A and B)	90	0	100
CE-F-42	AIR/EGR/3W/OC (catalysts A and B)	81	0	100
CE-F-45	AIR/EGR/3W/OC (catalysts A and B)	88	0	100
CE-F-60	AIR/EGR/3W/OC (catalysts A and B)	90	48	100
CE-F-61	AIR/EGR/3W/OC (catalysts A and B)	84	52	100
ADV-F-6	FBC/EGR/3W (catalyst A)	77	54	100
With factors for the addition of a clean-up oxidation catalyst and switched air injection				
ADV-F-6		100	100	100

*These were called 3-way catalysts by TK, but they function primarily as oxidation catalysts.

VI. Cost Analysis of Manufacuturers' Emission Control Systems

EPA Cost Estimates

The EPA costing methodology, as used in the CO Waiver Decision of September 5, 1979 [7] [29 at 53400], was revised to include responses to an EPA subpoena of August 8, 1979. (The subpeona requested prices that suppliers charge the automobile manufacturers for emission control devices or systems.) Table VI-1 represents the cost to the consumer of several emission control devices as derived from the subpoena responses. This table is not complete due to the delayed responses of many of the suppliers. In addition to a mark-up which accounts for the auto manufacturers' expenses, costs of most devices will vary based on production volume or sales volume to each auto manufacturer. Therefore, these are not absolute.

Table VI-1

Emission control device	EPA cost estimate in 1979 dollars
Air injection system	40
Carburetor:	
1 barrel	41
2 barrel	54
4 barrel	96
EGR system	13
Electric choke	6
Thermal vacuum switch (TVS)	3

Table VI-2 presents EPA estimates of cost of compliance with 3.4 vs 7.0 CO (due to lead time problems for certain emission control devices, separate estimates are necessary for 1981 and 1982). The changes in cost were calculated by individual engine size. These changes were based on the differences in emission control hardware between a) systems targeted to meet 7.0 CO, as described by each manufacturer in their applications and b) systems judged capable by EPA of meeting 3.4 CO, based on Monte Carlo results or successful 1980 certification of similar vehicles. (Cars which passed Monte Carlo often needed improved emission control hardware to do so, and these technological improvements were all costed in.) An engine size which was considered to fail in the Monte Carlo analysis was assumed to have no cost increase. Therefore, for TK in 1981, Table VI-2 represents the cost of compliance with 3.4 CO for some engine sizes and 7.0 CO for others.

As shown in Table VI-2, EPA did not find a change in cost for every engine size which passed the 0.41 HC, 3.4 CO, 1.0 NOx emission standard in the Monte Carlo analysis. (For example, certain Monte Carlo factors implied no change or a decrease in cost.) Engine sizes which are labelled "no data" in the Monte Carlo analysis are automatically assumed to have no change in cost.

The range in cost for Fuji indicates the effect of the switched air factor vs. aspirator factor for both engine sizes applying for waiver.

Table VI-2.—*EPA Estimate— Cost of Compliance With 3.4 CO*

Manufacturer	CID	3.4 vs. 7.0 CO in 1979 dollars 1981	3.4 vs. 7.0 CO in 1979 dollars 1982
Fuji	97	+91-+128	+91-+128
	109	+95-+137	+95-+137
Nissan	75	+35	+35
	85/91	0	0
	119	+12	+12
	146/168	+48	+48
	A	([1])	([1])
	B	([1])	([1])
Renault	85	+89	+89
Toyo Kogyo	70	−105	−105
	91	0 (fail)	+10
	120	0(fail)	+10

[1] No data.

Manufacturers' Cost Estimates

Table VI-3 presents the manufacturers' estimates of cost of compliance with the 3.4 CO standard over cost of meeting 7.0 CO [3 at 5-5] [2 at 1.5] [1 at 2]. Most manufacturers claimed some degree of confidentiality for their cost estimates, therefore, this table contains only that information which can be released. All costs are in 1979 dollars.

Table VI-3.—*Manufacturers' Cost Estimates*

Manufacturer	*Cost of compliance—3.4 CO vs. 7.0 CO*
Fuji	$80-$100
Nissan	$57-$104
Renault	(1)
Toyo Kogyo	[2]$50

[1] Confidential.

[2] Approximate.

VII. Driveability

Driveability is a specific criterion included in the evaluation of technical feasibility. As in the CO Waiver Decision of September 5, 1979, none of the manufacturers demonstrated that driveability was a crucial criterion on which a CO waiver should be granted.

This section includes a discussion of each applicants ability to maintain acceptable driveability in complying with the 1981–1982 emission standards.

Fuji

Fuji has not made an issue of driveability in their request for a waiver. Although Fuji has indicated that driveability problems exist with their SEEC-T system neither the SEEC-T or the oxidation catalyst systems are designed to meet the 3.4 gm/mile CO standard and no driveability data were presented to support their claims of driveability problems.

With respect to their FBC/3W/EGR system, which was designed to meet a 3.4 gm/mile CO standard, Fuji stated that "some driveability problems still remain which must be solved" [3 at 4–21].

> In addition we remain very concerned about the cold start driveability of these systems [FBC/3W/EGR]. We find that calibrations are very critical, possibly so critical that our internal driveability standards could not be met with production vehicles. Clearly a 7 gram CO standard would permit richer calibrations during warm up and would help alleviate cold start driveability problems [23 at 2].

In an effort to substantiate their claims for potential driveability problems with a 3.4 gm/mile CO standard, Fuji submitted a copy of a newspaper article [23 at 4] which stated that General Motors was not selling 1980 model year X-body cars with manual transmissions in California because of driveability problems, although they were selling these vehicles in the other 49 states. Fuji's reference to this article is not fully understood by the EPA technical staff in light of the fact that the 1980 California CO standard, at 9.0 gm/mile, is higher than the Federal CO standard, which is 7.0 gm/mile. It should be noted that this information comes by way of a newspaper article, not engineering data, and that two different emission control systems were involved. Additionally GM has stated that they expect "to get good driveability at either [3.4 vs. 7.0] standard" [33 at 182]. Fuji's application for a waiver did not include any driveability data. Also, at the hearings Fuji agreed that the following characterization of their position was correct: "* * * you're [Fuji] saying driveability has a potential for being a problem but at this time you don't know that it will be and *you're not claiming it will be* [emphasis added]." [5 at 149] Hardware improvement factors for a clean up oxidation catalyst with a switched AIR system and for an improved three-way catalyst should not adversely affect driveability.

Considering the prior characterization of their position, the EPA technical staff can only conclude that Fuji has not provided technical data to indicate that the driveability of their vehicles will be affected by a 3.4 CO standard as compared to a 7.0 CO standard.

Nissan

Driveability should not be a crucial issue in Nissan's ability to meet the 1981–1982 standards.

For their A-series engines, which include the 75, 85 and 91 CID engines, Nissan stated: "It is not possible to meet the 3.4 gr/mile CO standard when driveability is raised to an acceptable level in consideration of the warranty and recall requirements" [2 at 5.2.3].

These engines have been certified and are now being sold with calibrations that enable them to meet the 1981–1982 standards. The technical staff assumes that the driveability of vehicles being sold with the A-series engines is acceptable and that Nissan can therefore meet the 1981-1982 standards with acceptable driveability. Much of Nissan's early driveability data indicated that driveability was unacceptable when their emission targets were met. Nissan's emission targets are 0.26, 1.7 and 0.78 grams/mile for HC, CO and NO_x respectively. Because the Monte Carlo analysis, rather than Nissan's emission targets, is the criterion by which technical feasibility is determined, the technical staff rejects Nissan's claim that "It is not possible to meet a 3.4 gr/mile CO standard when driveability is raised to an acceptable level * * *" [2 at 5.2.3].

Instead, the technical staff judged that more appropriate emission targets should be set. It was determined that if Nissan's data indicated good driveability with emission levels at 80% of the 1981–1982 standards when multiplied by the deterioration factors of 1980 California durability vehicle AK749, this would satisfy the criteria for technical feasibility in terms of driveability. Vehicle AK749 finished its mileage accumulation with its emissions below the 1981–1982 emission standards. This method was used to approximate the Monte Carlo analysis. The Monte Carlo analysis itself could not be used because Nissan only submitted driveability data on development vehicles which had insufficient data for the Monte Carlo. Nissan did not submit driveability data on its durability vehicles.

Nissan submitted emissions data on two durability vehicles which met the 1981–1982 emission standards with A-series engines. Vehicles AK749 and A–883 had 91 CID and 75 CID engines respectively. All of Nissan's driveability data for A-series engines were from development vehicles with 91 CID engines. The deterioration factors from A–883 were not used because it did not have the same engine displacement as the vehicles which Nissan chose to submit driveability data on and the deterioration factors (d.f.) would have been lower, thus less conservative, had the d.f.'s from both vehicles been averaged.

On September 20, 1979 Nissan submitted data [13 at 3–25] on development vehicle AK714, which gave acceptable driveability while meeting EPA's aforementioned criteria. This vehicle had unacceptable driveability until Nissan recalibrated the choke and ignition timing and also controlled the ignition timing for quick catalyst light-off. Nissan also submitted data on other vehicles representing the A-series engines which had unacceptable driveability, but since Nissan did not submit the specific calibrations, EPA assumes that the improvements made on vehicle AK714 can also be applied to the other vehicles with A-series engines. Therefore, in the judgement of the EPA technical staff, it is technically feasible for Nissan to meet the 1981–1982 standards while maintaining acceptable driveability on their A-series engines. In addition, the use of an improved catalyst as simulated in the Monte Carlo, should not affect driveability.

For the 119 CID engine, Nissan has designed two emission control systems for the 1981–1982 standards, one using open-loop carburetion and the other using open-loop fuel injection. Although Nissan's initial submittal indicated driveability problems [2 at 5.2.2], a later submittal with new data [13 at 3–19] indicated that with a new device, a leaner choke setting, a leaner mixture, and an improved catalyst they were able to meet their emission target and maintain acceptable driveability. Also, Nissan indicated [2 at 5.2.2 and A.IV.5] that with fuel injection they were able to meet their emission target and maintain good driveability.

Nissan also submitted durability data [2 at 4.3.3] on a vehicle with a 119 CID engine with an EFI/FB/3W/light EGR control system designed to meet a 0.4 NO_x standard, but did not discuss driveability for this system. The use of dual walled exhaust pipe, as simulated in the Monte Carlo, should not affect driveability. In summary, the driveability data that Nissan did submit indicates that driveability will not be a major problem for the 119 CID engine.

Driveability for the 146 and 168 CID engines will be considered together because they have been historically certified as a single engine family. Nissan indicated that they could not meet their CO target of 1.7 grams/mile while maintaining acceptable driveability [2 at 5.2.4]. In a later submittal, Nissan submitted data [13 at 3–43] for a vehicle with advanced ignition timing during warm up which indicated that driveability was acceptable even when CO emissions were below 1.7 gms/mile. Also, three Nissan vehicles passed the Monte Carlo simulation with factors for an AIR system which, if used by Nissan, may allow them to further optimize calibrations for improved driveability and fuel economy. In light of the new data and possibilities available through the use of an AIR system, driveability should not be the crucial criterion in evaluating Nissan's ability to meet the 1981–1982 emission standards for the 146 and 168 CID engines.

Driveability for Nissan's "A" and "B" engines was not considered because they were deemed to be "no data" families.

The EPA technical staff concludes that Nissan has not shown driveability to be a crucial factor in their ability to meet a 3.4 grams/mile CO standard.

Renault

Renault discussed three emission control systems for their 85 CID engine, but did not submit any driveability data. These systems include their: (a) FBC/3W/EGR, (b) AIR/OC/EGR and (c) FBC/3W/OC/EGR/Switched AIR systems.

Renault claimed that the driveability of the three-way catalyst system would be unacceptable if the EGR rate were increased in order to comply with the 1.0 gm/mile NO_x standard, but no data were presented in support of this contention. [5 at 195] Renault also made claims of driveability problems with their oxidation catalyst system in order to comply with a 1.0 gm/mile NO_x standard. [4 at V/6] Again, Renault did not supply driveability data as requested in the guidelines.

Renault did not address driveability for the dual catalyst system, which is their only system designed to meet the 1981 standards. The EPA technical staff therefore can only conclude that driveability cannot be said to be a critical issue with respect to Renault's ability to meet the 3.4 gm/mile CO standard based on the information available.

Toyo Kogyo

In the Monte Carlo analysis of TK vehicles, only one of their three engines was projected to be able to pass the 0.41 HC, 3.4 CO, 1.0 NOx emission standard in 1981. Vehicles using all three engines were projected to be able to pass in 1982. None of those vehicles were projected to pass using the first choice TK emission control system.

TK did not provide driveability data in their waiver application or supporting documentation. The best indication of the driveability of TK vehicles is the qualitative evaluations presented in section II of reference 30. TK's first choice systems for 3.4 and 7.0 CO were all evaluated by TK as "good". The systems that passed in the EPA Monte Carlo analysis were not evaluated by TK. The first choice TK systems were AIR/EGR/3W/OC (open loop) for the conventional engines and AIR/3W/OC (open loop) for the rotary. Their passing systems were AIR/EGR/TR for the rotary and FBC/AIR/EGR/3W/OC for the conventional engines.

So the passing systems for the conventional engines differs from the first choice TK system only by the inclusion of feedback carburetion and the associated electronics and oxygen sensor. In the TK testimony [5 at 29 and 35], Mr. Suzuki suggested that TK was currently having driveability problems with their feedback carburetion. Again no quantitative data were provided.

In the absence of quantified driveability data from TK, the EPA technical staff can only conclude that any driveability problems being experienced by TK with their feedback carburetors may be due to the infancy of the TK program. Ford and GM both indicated that driveability of their vehicles using feedback control systems would not be affected by a 3.4 CO standard in 1981. [33 at 82 and 41 at 209]

The passing system for the rotary engine was not evaluated by Toyo Kogyo. The rotary engine using air injection and a thermal reactor was, however, rated as excellent by TK [30 at II–2]. Also, the passing system is a system currently certified (and presumably being sold). On this basis the EPA technical staff concluded that there is no evidence that the driveability of the passing system would be unaccepatable at either a 7.0 or 3.4 CO emission standard.

Driveability Summary

As discussed, each of the manufacturers indicated that driveability would be a problem in meeting a 3.4 CO standard, but none of these manufactures demonstrated that driveability would be a crucial criterion on which a CO waiver should be based.

VIII. Fuel Economy

Is there a change in fuel economy associated with going from 0.41 HC, 7.0 CO, 1.0 NO_x to 0.41 HC, 3.4 CO, 1.0 NO_x? This is an important issue in considering a manufacturer's request for a CO waiver from 3.4 to 7.0 gm/mi, especially with the fuel economy standards now in effect. There appears to be a disagreement between some of the manufacturers in their testimonies at the CO hearings regarding this issue.

Nissan and Fuji's testimony claimed negligible or no loss in fuel economy [5 at 91], [5 at 122] for meeting 0.41 HC, 3.4 CO, 1.0 NO_x versus meeting 0.41 HC, 7.0 CO, 1.0 NO_x. These agree with General Motors and Ford Motor Company statements in the earlier hearings [33 at 181], [41 beginning at 196]. In fact Nissan indicated that a 15 to 25 percent improvement in fuel economy (compared to their 1979 models) would be achieved in model year 1981 [5 at 91–92].

Renault indicated that they have not been able to achieve 3.4 CO and, as a result, they have not established a position concerning the fuel economy effects between the two CO standards.

The hardware improvement factors applied to these three manufacturers that were not already planned by the manufacturers (the planned improvements are presumably considered in their statements regarding fuel economy) are not expected to have a significant impact on fuel economy. The addition of air injection (AIR) is probably the most debatable in terms of a negative impact on fuel economy. Some manufacturers have estimated that a small loss in fuel economy is incurred with the use of AIR, but GM stated that in actual vehicle testing a loss in fuel economy could not be detected as a result of the addition of air injection [5 at 91–92 and 33 at 181–182].

Toyo Kogyo (TK), however, is claiming that they will experience a fuel economy loss of 5% in their piston engine in going from 7.0 to 3.4 CO [40 at 4]. This claim is questionable since TK claims that none of their systems have shown the capability to meet 3.4 CO in durability testing. Without fuel economy data at the 3.4 CO level, it would seem that TK's claim is based solely on their engineering judgement about their ability to calibrate their first choice systems to achieve the required CO standard. With the absence of comparative data, the EPA technical staff cannot agree with this judgement. TK also indicated that at either the 3.4 or 7.0 CO standard, fuel economy is improved over their 1979 model vehicles meeting a 15.0 CO standard.

TK reported that if the same open loop 3-way catalyst with air injection and EGR system used to meet the 1980 emission standards of 0.41 HC, 7.0 CO, 2.0 NO_x (with the conventional engines) is tailored to meet the 1981 standards of 0.41 HC, 3.4 CO, 1.0 NO_x, then a fuel economy loss of 5% should be expected [39 at 4]. However, if an open-loop three-way plus oxidation catalyst system with air injection and EGR system could be utilized, then as much as 10% fuel economy increase could be expected over the 1980 system calibrated for 3.4 CO. TK also claims that if this system were targeted for 7.0 CO an additional 5% fuel economy increase would result. TK also reported that their closed loop three-way plus oxidation catalyst system is very promising, and the most likely system to meet 0.41 HC, 3.4 CO, 1.0 NO_x [1 at 3], [5 at 14].

Fuel economy comparisons were made by the EPA technical staff on low mileage vehicles between the data provided by TK and what limited 1980 Toyo Kogyo certification data were available at the time of this analysis. These data are summarized in table VIII–1. These data show a fuel economy loss from 1.3 to 2.3% on vehicles with manual transmissions, compared to 1980 certification durability data at 4,000 miles (projected or calculated 4,000 mile fuel economy). One system, in fact, showed a 9.4% fuel economy increase. All vehicles equipped with automatic transmissions showed an increase in fuel economy from 2.4 to 11.3% over their 1980 certification counterpart. A closer look at the manual transmission data shows that the 2.4% fuel economy loss shown in table VIII–1 occurs when the inertia weight of the vehicle was increased by 250 pounds. This then would indicate that on vehicles of the same weight, a fuel economy loss of only 1.0 to 1.3% was evidenced. In the case of the automatic transmission data, increasing the inertia weight 250 pounds resulted in an 11.3% fuel economy *gain* over its lighter 1980 certification counterpart. It should again be noted that these are low mileage data, which were compared to limited certification data with a smaller engine displacement, but are the best data available at the present to perform this analysis. Although these data are rather limited, it does seem to indicate a potential for a net fuel economy gain for TK in 1981 compared to their 1980 vehicles.

TK supplied further data on an engine rather than model line basis [1 at 133]. These data again were separated with respect to transmission types, and are summarized in table VIII–2. These data, supplied by TK show a composite fuel economy range of 25.6 to 37.3 MPG. This is interesting data in that it exceeds the fuel economy standard of 24 MPG for 1982 (the last model year to which the waiver would apply) by 1.6 to 13.3 MPG or 4.4 to 55.4%.

TK reported that their 1980 rotary engine's fuel economy could be increased 10 to 15% by replacing the thermal reactor system with an open loop 3 way plus oxidation catalyst with air injection system. However, TK's data confirming this conclusion also shows that CO is increased above the 3.4 CO level. An EPA check of TK's contention is shown in table VIII–3. The fuel economy values in table VIII–3 were compared to TK's results of 21.6 MPG_c for vehicles with automatic transmissions and 22.9 MPG_c for vehicles using M5 transmissions and the open loop AIR/3W/OC emission control system. Clearly TK would experience a short term loss in fuel economy using the AIR/EGR/TR system for the vehicles using rotary engines compared to vehicles which would likely meet a 0.41 HC, 7.0 CO, 1.0 NO_x standard. A modest loss would also be incurred if the 1980 California system with air injection, EGR, and a thermal reactor were used on vehicles equipped with manual transmissions compared to the 1980 Federal models with automatic transmissions. The availability of feedback carburetion for the rotary in 1982 should result in fuel economy as good as or better than for the open loop AIR/3W/OC system. Thus, any loss in fuel economy that might be experienced by TK vehicles using rotary engines should be experienced for only one model year, and more importantly, would not appear to harm TK's ability to meet the fuel economy standards.

Table VIII-1*.—*Fuel Economy Comparison at Low Mileage of TK Research to 1980 Certification Date Vehicle: Mazda-GLC*

VIN	(CID) engine displacement	Transmission	Inertia weight	Emission control system	1980 EPA durability 4K certification MPG_u	Average 3.4 CO MPG_u	Percent differential MPG_u	Below 3.4 CO at low mileage?
ODUCP-1	86.3	M-5	2,250	OL-3 way catalyst/air pump/EGR	29.8			No.
CE-F-1, 3, 5, and 15	90.9	M-5	2,250	OL-3 way catalyst/air pump/EGR		29.4	−1.3	Yes.
CE-F-28, and 29	90.9	M-5	2,250	OL-3 way + ox/air/pump/EGR		32.6	+9.4	Yes.
ADV-F-1	90.9	M-5	2,250	CL-3 way-FBC/EGR		29.5	−1.0	Yes.
CE-F-17, 20, and 21	90.9	M-5	2,250	OL-3 way/air pump/EGR		29.3	−2.3	Yes.
CE-F-28, 29, 33, and 34	90.9	M-5	2,250	OL-3 way + ox/air pump/EGR		29.1	−2.3	Yes.
ODUCP-2	86.3	A-3	2,250	OL-3 way/air pump/EGR	24.7			No.
CE-F-2, 4, 6, 7, 8, and 16	90.9	A-3	2,250	OL-3 way/air pump/EGR		25.3	+2.4	Yes.
CE-F-30, 31, and 35	90.9	A-3	2,250	OL-3 way + ox/air pump/EGR		26.7	+8.1	Yes.
ADV-F-2	90.9	A-3	2,250	CL-3 way-FBC/EGR		29.5	+19.4	Yes.
CE-F-30	90.9	A-3	2,250	OL-3 way + ox/air pump/EGR		27.5	+11.3	No.

*TK—CO waiver application P. 113-133.
OL—Open Loop.
CL—Closed Loop.

Table VIII-2*.—*TK Fuel Economy Data on an Engine Basis*

		Fuel Economy							
		MPG_u		MPG_h		MPG_c		Percent over 1982 Cafe	
Engine/displacement (CID)	Emission control system	M-5	A-3	M-5	A-3	M-5	A-3	M-5	A-3
UC/86.3	OL-3 way (underfloor)/air/EGR.	29.8	26.0	40.0	32.0	33.7	28.4	37.5	18.3
MA/120.2		24.7	33.5	33.6	28.4	28.0	30.0	16.6	25.0
ES/90.9	OL-3 way (underhood)/air/EGR.	31.5	28.0	41.7	36.5	35.4	31.3	47.5	30.4
MA/120.2		24.3	23.6	33.3	28.6	27.6	25.6	15.0	4.4
ES/90.9	OL-3 way + ox cat (underhood and under floor)air/EGR.	32.6	27.6	43.1	38.8	36.6	31.7	52.5	32.1
MA/120.2		25.0	23.9	34.2	29.3	28.5	26.1	18.8	8.8
ES/90.9	FB carb + way/EGR	33.1	29.5	44.0	38.5	37.3	33.0	55.4	37.5
MA/120.2	3 way/EGR	25.5	24.5	34.5	31.0	28.9	27.1	20.4	12.9
MA/120.2	CL-single point fuel injection.	26.5		34.5		29.6		23.3	
MA/120.2	EFI/3 way/EGR	25.3	24.0	33.4	31.5	28.4	26.9	18.3	12.1

*TK—CO waiver application P. 133.

Table VIII-3.—*Fuel Economy of 1980 Model Year Vehicles Using Rotary Engines*

VIN	Eng	IV	Axle	N/U	Trans	HC*	CO*	NOx*	MPG_u	MPG_u	MPG_u
With Federal AIR/TR System											
OEREP-2	70	2750	3.91	58.1	A3	.208	2.53	1.39	16	24	19
OEREP-1	70	2750	3.91	58.1	M4	.170	3.70	1.05	16	25	19
OEREP-1	70	2750	3.91	48.0	M5	.202	4.26	1.17	17	28	20
With California AIR/EGR/TR System											
OEREP-4	70	2750	3.91	58.1	A3	.242	4.19	0.56	16	22	18
OEREP-3	70	2750	3.91	58.3	M4	.253	3.39	0.69	16	24	19
OEREP-3	70	2750	3.91	48.1	M5	.288	3.32	0.64	16	27	20

*Including deterioration factor.

TK is in agreement with the conclusion that closed loop systems offer improvements in fuel economy compared to their open loop systems as they stated that "closed loop dual catalyst with air injection plus EGR * * * has the highest potential to meet the fuel economy as well as emission requirements" [5 at 14]. This statement was made by TK in reference to conventional engines, but in the opinion of the EPA technical staff, it is equally true for the TK vehicles powered by rotary engines.

Since the thermal reactor system has already certified at the 0.41 HC, 3.4 CO and 1.0 NO_x standard, in 1980 certification it is evident that TK's position is a marketing rather than a technical issue. Since TK has already shown that they can meet 3.4 CO with their rotary engine, it is apparent that their request for a waiver to 7.0 CO on this engine is to allow their vehicles equipped with this engine to achieve better fuel economy resulting in stronger marketing leverage for TK.

In summary, none of the manufacturers have supplied sufficient data which show that a reduction from 7.0 to 3.4 CO results in a fuel economy penalty. TK may suffer a modest loss in fuel economy in 1981 for vehicles using rotary engines due to their inability to produce feedback air-fuel metering components. This loss could be recovered in 1982, and their ability to comply with the fuel economy standard in 1981 does not appear to be jeopardized. Therefore, EPA's position on this subject remains unchanged from the last hearing in that not inherent fuel economy penalty need be incurred in reducing the CO standard from 7.0 to 3.4 gm/mi.

IX. Lead Time

a. Fuji

Fuji Heavy Industries stated in its waiver application that they are basically committed to installing the three-way catalyst and electronically controlled carburetor system for all 1981 model year vehicles, regardless of the outcome of the waiver request for 7.0 g/mi CO. Considering costs and fuel economy at existing and projected emission standards, coupled with their existing and past development program, they say no other system provides a reasonable alternative for 1981. The development schedule for 1981 requires that final configurations and calibrations be selected by the end of October 1979. [3 at 5–9]

In the public hearings, however, Fuji stated that the performance of their first-choice system "has not been as good as expected", especially in terms of meeting the 1981 CO emission standard. [5 at 106] Two warm-up systems, (1) with high fast idle and ignition timing retard and (2) with low gear hold and ignition timing retard, have been developed to improve the original first-choice system for 1981 during the cold start phase. Warm-up system (1) will be used on manual transmission vehicles and warm-up system (2) on automatic transmission vehicles. [23 at 1]

Also stated at the hearings was that in addition to space limitations, they could not incorporate a larger or additional 3-way catalytic converter into their vehicles due to lack of lead time to change tooling, prove a new design and evaluate such a system. [5 at 133] But, according to Walter D. Biggers, Director, Subaru Technical Center, Subaru of America, there is enough room for an additional oxidation catalyst if they can just provide enough ground clearance for the catalyst heat shields. [5 at 121]. It is the opinion of the technical staff that the heat shield problem can be resolved for the 1981 model year. Testimony given by catalyst manufacturers at the hearings indicate an excessive availability of applicable oxidation catalysts on the market for 1981. [37 at] and [38 at 89] With access to these catalysts, changes in tooling and design would be minimal and durability testing and evaluation are already included in the certification process. Therefore, if Fuji were to apply a three-way plus oxidation catalyst system with an aspirator in between to lower emissions for 1981, it would still seem possible in terms of lead time. Also in the hearings, with regard to the "A-1" three-way catalyst system, they claimed that they could not install an air pump due to lack of space and lack of lead time to modify the engine layout. Other reasons given were that air pumps are too noisy, they drain power and are too expensive. [5 at 128] Based on photographs submitted by Fuji, it appears that modifications to engine layout would not be so significant as to preclude the use of air pumps on their 1981 models. [40] If no other space is available the air pump could be installed in place of the air conditioning compressor.

b. Renault

Renault has proclaimed that their two catalyst (3-way and oxidation) system with Ford ECU feedback carburetor, air pump and EGR is their first choice system. [4 at V/5] Problems with this system include lack of space for a dual-bed catalyst and poor efficiency of the oxidation catalyst (which for space reasons is located far from the engine). For these reasons Renault states that their first choice system, in its present stage of development, is not able to meet the 1981–82 standards. It seems feasible however, barring space contraints, that Renault could place the oxidation catalyst closer to the engine and achieve better efficiency. In the opinion of the technical staff they have not substantiated that it is not possible to relocate the catalyst further upstream. The problems involved with using the vertical mount position may be soluble, and Renault did not discuss the possibility of locating the catalyst between the vertical mount (downpipe) position and any location in front of the current catalyst position.

c. Toyo Kogyo

Although they project better fuel economy and lower CO emissions with a closed loop system, Toyo Kogyo has stated that their first choice system for their conventional engines is an open-loop dual catalyst configuration with air injection and exhaust gas recirculation. This is their C–1 system. Two other systems which are continuing development to comply with the 1981 standards are C–2; closed loop three-way catalyst plus EGR and C–3; closed loop dual catalyst plus EGR. [5 at 12–13]

Due to lack of reliability of the O_2 sensor, the C–3 system is currently experiencing developmental difficulties. [5 at 37] Satisfactory results are not expected from their oxygen sensor development program until April 1981 unless Toyo Kogyo can achieve significant success with their Step II Engine Dynamometer Test. This step of the program is scheduled to be completed in May, 1980. Six kinds of oxygen sensors, from three suppliers, have been evaluated thus far, and most of the samples in ordinary running showed no deterioration such as probe breakage or output drop. However, under high-speed heavy-load driving conditions where the oxygen sensor probe is exposed to high temperature and a reduction atmosphere, or in a cyclic test at low and high speed operations, "intolerable output drop or probe breakage was detected". [30 at III–2]

Also holding up the C–2 and C–3 systems is the development of the feedback carburetor. Toyo Kogyo's feedback carburetor development started in 1977 in a joint program with the carburetor manufacturers. Three systems (the air bleed solenoid, the fuel metering rod solenoid and the fuel control solenoid systems) are currently being studied. By April, 1980, evaluation of these systems will be complete and a first choice system will be selected. Reliability, compliance with high altitude emission regulations and full-scale vehicle durability are all scheduled to be accomplished by March or April, 1981. [30 at III–3] At the public hearings, Toyo Kogyo stated that they will have the feedback carbutetor and O_2 sensor components ready for the 1982 model year. However, further adjustments that may be necessary to the total system make 1983, Toyo Kogyo says, "a more comfortable dateline if we have to commit to something". [5 at 43] If they can have the necessary components in time, and system adjustments are their only constraints, it is EPA's contention that the feedback carburetor system could be used by Toyo Kogyo in 1982.

d. Nissan

Nissan requests a waiver for two years lead time to develop, simplify and refine their current systems, especially in the areas of driveability and fuel economy. They state in their application that if it is necessary to keep CO emissions under 3.4 g/mile, there is not enough time left to perform part durability and system reliability tests before the decision deadline. [2 at 3.1, 5.5.1]

EPA has received responses from Nissan to some of their public hearing questions concerning lead time for various components. These include responses concerning electronic fuel injection, advanced electronics, and start-up air injection on three-way catalyst vehicles.

Electronic fuel injection (EFI) is said to be available for all engines except the A-series engines [5 at 98], but when warranty and recall requirements are considered, Nissan cannot guarantee that this system will clear the CO standard under different types of actual use. [13 at 5.2.2] Nissan's Electronic Concentrated Engine Control System (ECCS) in the 6 cylinder engine was introduced into the domestic Japanese market in June, 1979.

Nissan says, for the 6 cylinder engine, that ECCS is available for a part of the 1981 U.S. models since this is already done in Japan. [13 at 38] Air pumps and start-up air injection systems on three-way catalyst vehicles are compenents that Nissan has developed and used in the past. However, with their present configurations, especially the EFI engines, they must redesign due to lack of space. Redesigning, they say, requires a lead time incompatible with the time necessary to be ready for the 1981 model year. [13 at 42–44] It is unclear from the photographs sent to EPA [13 at 43–53] whether or not there is enough space to install an air pump on the engines shown. However, from the schematic diagram [13 at 50] for the L6E engine (model 280ZX), it appears entirely possible that space for an air pump exists. If the pump is moved to the side or down slightly, interference with the BCDD control valve is avoided and at most a small adjustment of the air conditioning compressor location would be needed. If necessary, the air pump could be installed in place of the air conditioning compressor. Therefore, since the technology is available and the necessity for time consuming redesign is unapparent, we conclude that it is possible for Nissan to use air pumps on their 146/168 CID engines in 1981.

An additional system involved in lead time considerations is dual-walled exhaust pipes. At present, Nissan uses dual-walled exhaust pipes for 1980 Z20E and L6 series engines, and will also use them in the same engine series for 1981. They said they will also use them for the 1981 Z20S and A-series engines if necessary. [13 at 13].

X. References

(1) Toyo Togyo Co., Ltd. *Application for Waiver of 1981 and 1982 CO Emission Standard for Passenger Cars*, July 1979.

(2) Nissan Motor Co., Ltd. *Application for Waiver of the 1981 and 1982 CO Emission Standard for Light Duty Vehicles*, August 1979.

(3) Fuji Heavy Industries, Ltd. *Waiver Request of Carbon Monoxide Standard for 1981 and 1982 Model Year Light-Duty Vehicles*, September 1979.

(4) *Renault Application for Waiver of 1981 and 1982 Carbon Monoxide Emission Standard*, September 1979.

(5) *Transcript of Proceedings—Environmental Protection Agency—In The Matter of: Public Hearing On Applications for Waiver of the 1981 and 1982 CO Emission Standard for Light Duty Vehicles*, dated September 12, 1979 by Acme Reporting Company.

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(7) LeRoy H. Lindgren, *Cost Estimations For Emission Control Related Components/Systems and Cost Methodology Descriptions*, EPA–460/3–78–002, March, 1978.

(8) Letter and Enclosures to Mr. Benjamin R. Jackson (Mobile Source and Noise Enforcement Division of EPA) from Mr. Teruo Maeda (Nissan Motor Company, Ltd.) dated July 11, 1979.

(9) "Nissan's Statement at the Public Hearing on Applications for Waiver of the 1981 and 1982 CO Emission Standard for Light Duty Vehicles," July 12, 1979.

(10) "Corrected Pages to Supplemental Documentation Submitted by Nissan to EPA

on July 9, 1979 in connection with Hearing on Application for Waiver of the 1981 and 1982 CO Emission Standard for Light-Duty Vehicles," July 12, 1979.

(11) *Supplemental Documentation for the Public Hearing on Applications for Waiver of the 1981 and 1982 CO Emission Standards for Light-Duty Vehicles,* Nissan Motor Co., Ltd., July, 1979.

(12) Letter and Enclosures to Mr. Charles N. Freed (Mobile Source and Noise Enforcement Division of EPA) from Mr. Teruo Maeda (Nissan Motor Co., Ltd.), July 23, 1979.

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(14) "Nissan's Statement at the Public Hearing on Applications for Waiver of the 1981 and 1982 CO Emission Standard for Light-Duty Vehicles," September 12, 1979.

(15) Letter and Enclosures to Mr. Benjamin R. Jackson (Mobile Source and Noise Enforcement Division of EPA) from Mr. Teruo Maeda (Nissan Motor Co., Ltd.), September 12, 1979.

(16) Fuji Heavy Industries, Ltd. *Additional Information Requested by EPA at the Waiver Hearing on September 12, 1979,* September 18, 1979.

(17) Renault. *Application for Waiver of 1981 and 1982 Carbon Monoxide Emission Standard Supplementary Information,* September 1979.

(18) Renault. *Additional Information Requested by EPA at the September 18, 1979 Public Hearing,* September 24, 1979.

(19) Letter and Enclosures to Mr. Charles N. Freed (Mobile Source and Noise Enforcement Division of EPA) from Mr. Teruo Maeda (Nissan Motor Co., Ltd.), September 28, 1979.

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(28) Letter and enclosure to Mr. Benjamin R. Jackson (Mobile Source Enforcement Division of EPA) from Mr. Joseph H. Povey (Matthey Bishop, Inc.), August 10, 1979.

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(30) Letter to Marvin B. Durning (Mobile Source Enforcement Division of EPA) from Masatoshi Ogata (Toyo Kogyo USA Representative Office), September, 1979.

(31) Toyo Kogyo Co., Ltd. *Response to the Questionnaire raised by EPA Ann Arbor on our CO Waiver Request for 1981 and 1982 Model Years,* September 28, 1979.

(32) *Application for Waiver of the 1981 and 1982 CO Emission Standard for Light Duty Vehicles,* Volkswagen AG, July, 1979.

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(35) *B.L. Cars Ltd., Application for Waiver of 1981 and 1982 Carbon Monoxide Emission Standards,* June 1979.

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(43) Letter and enclosures to Mr. W. Pidgeon (Emission Control Technology Division of EPA) from Ms. Marilyn Mehr (Renault) dated October 12, 1979.

(44) Letter and enclosures to Mr. Glen Unterberger (Mobile Source Enforcement Division of EPA) from Ms. Marilyn Mehr (Renault) dated September 24, 1979.

(45) Letter and enclosures to Mr. Glen Unterberger (Mobile Source Enforcement Division of EPA) from Ms. Marilyn Mehr (Renault) dated September 28, 1979.

Appendix B.—Summary of Public Health and Air Quality Analyses as Related to Light Duty Vehicle CO Waiver Applications

Review of CO Air Quality and Health Effects Data

Data concerning the effects of a two year waiver of the light-duty vehicle (LDV) carbon monoxide (CO) emission standard have been obtained from various sources. These sources include: EPA's Office of Air Quality Planning and Standards (OAQPS); EPA's Office of Mobile Source Air Pollution Control (OMSAPC); Ford Motor Company; General Motors; and Chrysler. The data presented here consider the effects on air quality and public health of waiving the Congressionally mandated 1981 LDV CO emission standard of 3.4 grams/mile to 7.0 grams/mile for the 1981 and 1982 model years.

In our consideration of public health issues for this waiver request, we have assumed that the current EPA National Ambient Air Quality Standards (NAAQS) for CO of 35 ppm for a one-hour average and 9 ppm for an eight-hour average determine air quality levels adequate to protect public health. The NAAQS CO standard is designed to protect public health. The effect of a CO waiver on ambient air quality will thus also be considered in this paper as determining the effect of a CO waiver on public health.

This report will serve as a review of the air quality data presented in manufacturers' CO waiver submissions to EPA as well as the results of several of EPA's own air quality studies.

1. EPA—OAQPS Analysis. OAQPS has performed four successive analyses of the air quality impacts of waiving the 3.4 gram/mile LDV CO emission standard [*1 2 3 4*). These analyses used rollback models to predict the differences in air quality for future years in various Air Quality Control Regions (AQCR's) as a result of different CO Emission standards. Neither of the first two of these analyses considered the impact of a two year waiver but considered *either* a 3.4 gram/mile *or* a 7.0 gram/mile CO standard for 1981 and later years. This discussion will deal only with the data contained in the last of these four analyses as it is the most comprehensive in that it delas with the effects of a two year waiver and predicts the air quality effects on a year to year basis. These analyses includes scenarios combining three possible emission control system penetration rates, three emission rates, and three possible in-use deterioration rates. A total of 186 unique emissions scenarios for CO were analyzed and air quality projections were made for 19 AQCR's for the years 1981 through 1995. Specific details and assumptions made in the OAQPS analysis include the following:

(a) The analysis was done for 19 AQCR's. Criteria for choosing the 19 AQCR's were that appropriate CO data were available, the AQCR's had some of the most severe CO problems, the AQCR's were not in California or at high altitude where different emission rates would be necessary, and these AQCR's had been used frequently in the past by OAQPS. The 19 AQCR's are:

Birmingham
North Alaska
Clark-Mohave
Phoenix-Tucson
Hartford-New Haven
NY-NJ-Conn.
Philadelphia
National Capitol
E. Washington-N. Idaho
Chicago
Indianapolis
Kansas City
Baltimore
Boston
Minneapolis-St. Paul
Central New York
Portland
S.W. Pennsylvania
Puget Sound

(b) OAQPS's Linear Rollback Model was used to predict the reduction in ambient CO concentrations, the number of AQCR's above the 9 ppm, 8-hour NAAQS, and the total number of 9 ppm, 8-hour CO NAAQS violations in the 19 AQCR's in 1981 through 1995.

(c) The 186 CO emissions scenarios are those used in the March 9, 1979 memo from Charles L. Gray to Robert E. Neligan.(*5*)

(d) One half of the 186 scenarios assumed the following CO emission standards:

1977-79—15.0 grams/mile
1980—7.0 grams/mile
1981-95—3.4 grams/mile

The other half of the 186 scenarios assumed the following:

1977-79—15.0 grams/mile
1980-82—7.0 grams/mile
1983-95—3.4 grams/mile

(e) Each scenario assumed one of the three possible generic emission control system penetration rates. The resulting possibilities are:

(1) 100% 3-way plus oxidation catalyst systems (possible system for 3.4 grams/mile CO and 1.0 grams/mile NO_x).

(2) 100% 3-way catalyst systems (possible system for 7.0 grams/mile CO and 1.0 gram/mile NO_x).

(3) 10% 3-way catalyst systems, 80% 3-way plus oxidation catalyst systems, and 10% oxidation catalyst plus air pump systems (possible systems for 3.4 grams/mile CO and 1.0 gram/mile NO_x).

(f) Each scenario assumed one of three *certification* deterioration factors (DF's). The DF values possible were 1.0, 1.5, and 2.0 and the DF value chosen determined the CO emission level of new (zero mile) vehicles. Certification DF's are 50,000 mile emission levels of prototype vehicles (which must meet the emission standards) divided by 4000 mile emission levels. These DF's are then used to determine what emission levels new (zero mile) vehicles must meet.

(g) For each exhaust treatment system each of three possible *in-use* deterioration rates is applied. The primary deterioration rate is that reported by EPA in Table I-1 of its "Mobile Source Emission Factors" document (*7*) and referred to as "AP-42." The other two deterioration rates for which scenarios are calculated are the "AP-42" rate divided by two and a zero deterioration rate.

(h) A one percent growth rate compounded annually from mobile source CO was assumed to result from increased vehicle miles traveled (VMT) for each AQCR.

(i) Stationary source CO emissions were projected to grow at a rate of 3.2 percent compounded annually.

(j) The CO base year concentration or "design value" was selected to be the highest second highest 8-hour concentration from the period 1974 through 1976. A background concentration of one ppm was also assumed for each region.

(k) The 1976 base year emissions inventories were taken from the EPA National Emissions Data System (NEDS). Stationary source CO emissions from NEDS are included under electric generation, industrial, or miscellaneous sources.

(l) A stationary source contribution factor of less than 1.0 is used for each CO stationary source category. These factors account for the fact that CO "hot spots" are typically located in areas of high traffic density which are not usually associated with significant stationary sources of CO. CO stationary source contribution factors of 0.0 for power plants, 0.1 for industrial sources, and 0.2 for area sources were selected after considering the results from dispersion models for power plants and other industries, and review of the relationship between traffic density and CO levels in several situations.

(m) Control technology assumptions for stationary source CO control used in the OAQPS analysis are those described in the Three Agency Study. (*6*)

For each scenario the following projections are calculated for the years 1981 through 1995.

(a) The highest second highest 8-hour concentration of CO for each AQCR.

(b) The number of violations of the 9 ppm, 8-hour CO NAAQS for each AQCR.

(c) The average percent reduction in the highest second highest 8-hour CO concentration for the 19 AQCR's in 1981 through 1995 from the average 1976 concentration.

(d) The number of the 19 AQCR's in violation of the 8-hour CO NAAQS.

(e) The sum of the total number of 8-hour CO NAAQS violations projected to occur in the 19 AQCR's.

As only a limited amount of AQCR's are used in these projections, they must be viewed carefully. The data presented in Table 1 and Reference 4 are the results of projecting either a 3.4 or 7.0 gram/mile CO LDV emissions standard for the years 1981 and 1982 and then a 3.4 gram/mile CO LDV emission standard for the succeeding years. Within the constraints of these projections, both the average percent reduction in the highest second highest 8-hour CO concentration for the 19 AQCR's and the sum of the total number of 8-hour CO NAAQS violations in the 19 AQCR's are representative of what air quality trends that one could expect to see as a result of a two year CO waiver. The number of AQCR's predicted to show eight-hour NAAQS violations also serves as a comparison of the scenarios in the OAQPS data. two scenarios have been chosen for comparison of the effects of the waiver on the above mentioned parameters.

These scenarios as summarized in Table 1 were chosen to represent first a possible reasonable assumption of what systems and deteriorations might be expected for vehicles meeting 3.4 or 7.0 grams per mile standards and second, what might be considered to be a "worst case" comparison looking for maximum differences between the two (but excluding the zero deterioration rate scenarios which although they showed greater improvements in air quality, were judged to be less probable). In 1985, with a CO waiver across the board, this analysis indicates that from 4 percent to over 30 percent more violations of the eight-hour CO NAAQS could occur in the 19 AQCR's analyzed.

Table 1.—*Air Quality Projections*

Scenario	1981	1982	1983	1984	1985
Nominal Case					
Waiver:[1]					
(2)	19	25	30	36	41
(3)	16	16	14	12	12
(4)	660	530	410	310	230
Standard	7.0	7.0	3.4	3.4	3.4

Table 1.—*Air Quality Projections*—Continued

Scenario	1981	1982	1983	1984	1985
Nominal Case					
No waiver: [5]					
(2)	20	25	31	36	41
(3)	16	15	14	12	12
(4)	650	520	400	300	220
Standard	3.4	3.4	3.4	3.4	3.4
Possible Maximum Difference Case					
Waiver: [6]					
(2)	19	24	30	35	40
(3)	16	16	14	12	12
(4)	660	540	420	320	240
Standard	7.0	7.0	3.4	3.4	3.4
No waiver: [7]					
(2)	20	25	32	38	44
(3)	16	15	14	12	11
(4)	650	510	380	270	180
Standard	3.4	3.4	3.4	3.4	3.4

[1] 100% 3-way catalyst system, AP-42 deterioration rates, certification DF=1.5.

[2] The projected average percent reductions of the highest second highest CO reading over the 19 AQCR's.

[3] The number of the 19 original AQCR's predicted to show 8-hour NAAQS violation.

[4] The total number of 8-hour CO NAAQS violations in the 19 AQCR's.

[5] 100% 3-way plus oxidation catalyst stystems, AP-42 deterioration rates, certification DF=1.5.

[6] 100% 3-way catalyst system, AP-42 deterioration rates, certification DF=1.0.

[7] 100% 3-way plus oxidation catalyst systems, AP-42/2 deterioration rates, certification DF=2.0.

2. SRI-EPA CO "Hot Spot" Report. The Atmospheric Sciences Center of SRI International has in preparation for EPA a draft report entitled "Analysis of Pollutant and Meteorological Data Collected in the Vicinity of Carbon Monoxide 'Hot Spots.' " (*8*) The SRI research program currently has the following objectives:

a. Identify the contribution of carbon monoxide (CO) and hydrocarbon (HC) emissions from local sources versus the contribution from regional sources, as determined by the total concentrations measured around urban roadways in areas where concentrations are greatest (i.e., "hot spots").

b. Estimate the percentage of vehicles in different operating categories—e.g., hot start, cold start, and stabilized, as well as traffic mix, volume, speed, and idletime data.

The analysis in the draft report addresses only the first objective. The other objective will be dealt with in another report.

For this study four cities (San Jose, Seattle, Phoenix, and Chicago) were chosen to represent a broad range of climatological areas and different vehicle operating conditions. The area chosen for HC and CO sampling within each city was also selected to provide diverse conditions. The San Jose site was in the vicinity of a congested suburban intersection with considerable commercial development in the immediate area. The Seattle and Chicago sites were in heavily congested downtown areas. The Phoenix site was near numerous government buildings and provided data from an area where there is a simultaneous emptying of many office buildings. The sites were also chosen to be sites expected to show "hot spot" or high CO levels from vehicle traffic. The sites picked in Seattle, Phoenix, and Chicago were ones known to have previously violated the NAAQS. Preliminary measurements at the San Jose site showed that high CO levels were also present at that location.

Within each site area the researchers wished to determine what fraction of the ambient CO level was from the surrounding area and how much from local (motor vehicle) sources. To do this ten monitors were placed at various locations within each site. Some were placed upwind, on tall buildings, or set back from local streets. These monitors would represent the areawide or background concentrations. Other monitors were placed closer to the local sources so that the street level or local source contribution could be determined. The area monitors could, even though they were placed well away from the local monitors, still be influenced by local sources. To minimize this effect, the background concentration was chosen to be the lowest of the measured values of the area monitors.

The report presents, at great length, all of the data for both CO and HC at each of the ten monitors in each of the four sites. These data are also presented in terms of one- and eight-hour CO and HC averages for each site.

The San Jose site shows ten violations in seven days of the 9 ppm, eight-hour CO NAAQS. All of the readings resulting in violations occurred at monitors downwind of the intersection during light wind (2.1 m/s ave.) conditions. The local contribution to ambient CO levels during periods when the CO concentration was above 9 ppm (the eight-hour CO NAAQS) ranged from 62 to 98 percent and averaged 80 percent.

The Seattle site had five eight-hour CO NAAQS violations in the seven day period. Three of these violations were similar to the San Jose violations with relatively high CO concentrations being seen at all the local monitors. The other two violations were more widespread with high CO concentrations at all local and two of four background monitors. This indicates that these high CO concentrations were widespread and not restricted to the immediate study area or to "hot spots." The authors point out that these two violations occurred following heavy traffic volume over a fairly wide area and this probably accounts for the high background levels.

Four eight-hour CO NAAQS violations occurred in the seven days of sampling at Phoenix. They all occurred during eight-hour periods ending at about one to three a.m. During NAAQS violations local CO contributions ranged from 18 to 59 percent with a 35 percent average. This is a relatively small amount. The authors feel that the high night time and low local CO concentrations may be explained by recirculation of air that passed over the city during peak emission periods moving back during the early morning and causing violations at the test site.

Chicago data showed only two eight-hour CO NAAQS violations. Both represented very high local contributions ranging from 79 to 97 percent with a 86 percent average. These are characteristic of classical "hot spot" violations.

The authors conclude that they found important differences between various eight-hour CO NAAQS violations. San Jose and Chicago had the expected high local contributions. In Phoenix all violations occurred when local contributions were relatively small. The Phoenix location could not be classified as a "hot spot." Seattle had several violations that could be classified as "hot spot" violations but several others that were area wide violations. The significance of this work is that it shows that it is not always valid to consider CO just a localized problem occurring in the central business district. It could be that with increased total vehicle miles traveled that CO becomes more of an areawide problem.

3. General Motors Submission. General Motors has made a number of comments regarding public health and air quality data in their CO waiver application, in their testimony, and in their later submissions. They maintain that the 3.4 gram/mile standard is not needed for protection of public health. We will address their comments individually.

a. Present CO Air Quality Standards Provide A Substantial Margin of Safety. EPA has stated on numerous occasions that the present one- and eight-hour NAAQS for CO is designed to adequately protect public health. There is controversy in the scientific literature over what ambient CO levels cause what carboxyhemoglobin (COHb) levels in the blood. The CO NAAQS is designed to prevent blood COHb levels above 2.0 percent saturation in normal populations. According to GM, COHb levels of 1.5 percent are associated with eight-hour CO NAAQS levels. GM apparently feels that this difference represents too great of a margin for safety. In determining the appropriate margin of safety, EPA must consider the relationship between ambient CO and blood COHb levels, the effects of altitude, the impact on highly sensitive individuals such as pregnant women, fetuses, persons with angina, anemic individuals, persons with chronic obstructive pulmonary disease, etc. which represent significant portions of the population. In taking into account these factors the margin of safety does not appear inappropriate.

b. Estimation of a CO Emission Standard to Protect Public Health. EPA does indeed find that in-use emission rates from the average vehicle exceed the applicable standards by gross amounts for most of the life of the vehicle. This is partly why recent air quality models based upon MOBILE1 deterioration rates show the need for lower CO emission standards.

c. Important Assumptions in Calculation of the CO Standard.

(1) Emission Rates: GM has, in this section, attacked EPA's in-use emission rates as unrepresentatively high and not in agreement with data from the EPA Emission Factor Surveillance Program. They also claim that in-use emission rates for future vehicles will be less than that of present vehicles. The reason given for this is EPA's "parameter adjustment" regulations which are already figured into future year vehicles in MOBILE1.

EPA is in the process of reviewing in-use vehicle emission rates. The emission rates currently being used in MOBILE1 are, as was pointed out by GM in their oral presentation, close to actual in-use measurements for vehicles with 40,000 miles or less. GM contends that data show a leveling off of emission deterioration after 20,000 to 40,000 miles. EPA has claimed that continued deterioration with age is justifiable as emissions system tampering increases with vehicle age. (*9*)

GM, in their oral presentation, made a significant point of how EPA has, in MOBILE1, used a deterioration factor (DF) of 1.7 for 1968–1974 and 1975–1979 vehicles but has used a DF of 3.7 for 1980 and later model year automobiles. GM stated that with "parameter adjustment" regulations and future technologies they would expect future in-use emissions to be much lower. EPA, in fact, has assumed this and GM's interpretation is misleading. First, the DF of 1.7 they refer to for 1968–1974 model year vehicles corresponds to a deterioration rate, as used in MOBILE1 and Reference 6, of 6.15 grams/mile of deterioration per 10,000 miles. The DF of 1.7 GM refers to for 1975–1979 model year vehicles corresponds to a deterioration rate of 2.80 grams/mile per 10,000 miles. The DF of 3.7 GM refers to for "future models" actually in MOBILE1 is applicable only for 1980 model year vehicles and corresponds to a deterioration rate of 2.3 grams/mile per 10,000 miles. For 1981 and future years MOBILE1 assumes a deterioration rate of 2.0 grams/mile per 10,000 miles. It is thus clear that EPA and its MOBILE1 model assume decreasing deterioration rates on a gram/mile basis for newer technology vehicles. The deterioration factors or DF's that GM refers to are not a true reflection of actual vehicle deterioration. The DF's that GM discusses are 50,000 mile emission rate divided by 4000 emission rate. The DF of 1.7 that GM suggests using for future vehicles (Figure 6 of their oral presentation) corresponds to an unrealistic in-use deterioration rate of only 0.75 grams/mile per 10,000 miles for CO.

GM submitted additional information concerning EPA and GM tampering surveys to EPA (*10*) in response to questions asked at the CO Waiver Public Hearing. GM claims that its interpretation of EPA's tampering report shows that EPA's contention that tampering increases with car age is fallacious. They claim that tampering, both in the EPA and GM surveys, grows to a certain level and then levels off after a certain number of miles. They claim that in the EPA data (shown in Figure 1 of Attachment C of their additional submission) this plateau has been reached for the 1973 and 1974 vehicles. They neglect to mention that many 1974 vehicles had relatively primitive emissions control systems and are recognized as a low point in LDV fuel economy ratings and *may* not be validly used to extrapolate other vehicle year's emissions. The GM Customer Car Emission Control Modification Survey that GM mentions does show a tapering off of emission control system tampering with vehicle mileage but again details of the GM study are very sketchy, and cannot be used as a basis to modify the in-use deterioration rates.

(2) Growth Projections: GM presented their concern over EPA's use of a one percent, compounded annually *center city* vehicle miles traveled (VMT) growth rate as being unrealistically high. They claim that birth rates have fallen to replacement only levels and that many mature center city areas are already saturated with traffic. Figure II.C.1. of the GM submission shows U.S. human population growth projections with both a 1.14 percent compounded growth rate (1970–71 growth rate) and the U.S. Bureau of the Census, Series II projection (about a 0.75 percent compounded growth rate). Thus GM assumes that a 0.75 percent growth rate corresponds to what is referred to as "replacement levels." Figure II.C.2. of GM's submission shows VMT growth rate projections for four large metropolitan areas which are also CO non-attainment areas. The cities and their VMT growth rate projections are: Phoenix: 2.5 percent; Los Angeles: 0.75 percent; Chicago: 0.75 percent; New York: 0.35 percent.

(3) "Base Year" Air Quality Data: GM criticized EPA's use of what they consider to be "erroneously high" base year air quality levels in the "Walsh/Lillis" study.(*1*) Revised air quality projections have been made by EPA(*3, 4*) for a more recent "base year" (1976) and only two (of 19) AQCR air quality levels were found to have lower base year concentrations of CO.

d. Historical CO Air Quality Trends. Figure 11.D.1. of GM's submission reportedly shows how CO levels have dropped from about 13 ppm to 5 ppm over the years 1969 to 1977 at the 45th Street monitor in New York City. GM feels that these data reflect a nationwide trend downward in CO levels due to control of motor vehicle emissions. They claim that similar downward trends in CO concentrations have been shown in other large metropolitan areas. GM claims that EPA's rollback model predicts only a 13 percent rather than a measured 59 percent reduction in Manhattan. The Manhattan site which GM chose to measure CO reductions corresponds to the site where EPA has also found the greatest CO reductions. EPA has found a much lower average reduction in ambient CO for this same time period when averaged over all sites. Unfortunately, Figure 11.D.1. can be characterized as highly questionable as it reports data taken with several instruments, the first of which shows no apparent downward trend and a large amount of scatter.

e. Effect of Two-Year Waiver on Air Quality. GM's position is that from their interpretation of air quality data a 7 or 9 gram/mile LDV CO emissions standard is sufficient to achieve the CO NAAQS. They would like to see a permanent relaxation of the 3.4 gram/mile standard. Likewise GM feels that a two year waiver will have no effect on the attainment of the CO NAAQS. GM claims that by using EPA's rollback model with the assumptions they have questioned (*1*) they only calculate a maximum total fleet emissions rate 1.96 percent lower in 1987 (the year when there is expected to be the maximum effect) if the waiver is not granted. They further calculate that granting the CO waiver will increase ambient CO levels in Chicago by 0.28 ppm and Spokane by 0.16 ppm, which they feel to be two typical cities, in 1987. They call these levels "insignificant" in view of the uncertainities present in the rollback calculations and assumptions.

f. Cost of Hours of Disability. GM criticized EPA's projection of the increased personhours of disability related to cardiac disease (from Reference *1)* as being insignificant. It should be mentioned that the approximately 5,000 personhours of disability projected for the year 1990 by the model are only for the 26 AQCR's and only related to cardiac disease. The so called "Three Agency Study"(*6*) made similar projections of the health consequences of alternate CO emission standards. Although these projections are also dated and apply to slightly different emission standards for slightly offset years, they also project a significant number of additional personhours of disability associated with a higher CO emissions standard.

4. Ford Motor Company. Although Ford has not applied for a CO waiver, they have kept their option open to do so. They have, however, submitted data and reports which they claim show that the 1980 model year 7.0 grams/mile LDV CO emissions standard is sufficient to achieve the 9 ppm eight-hour CO NAAQS and that a further tighting of the vehicle emission standards is not necessary to protect the public health. Ford has submitted specific reports dealing with each of their comments. These reports are discussed below.

a. Air Quality Effects of a CO Waiver. In Ford's attempt to "better" analyze the CO air quality data they duplicated the projections of Lillis (from Reference 1), extended that model to include the effects of a two year CO waiver, and analyzed seasonal air quality and temperature data from various locations. Although no changes were made in its theoretical basis, EPA has since revised and updated the data inputs into the modified rollback model which Ford used in their modeling efforts. This reduces the ability to compare the two analyses.

Ford's modeling results, using input assumptions from Reference 1, showed small air quality differences due to a CO waiver. Projected air quality, rounded to the nearest ppm, indicated a difference in 1985 of no more than one ppm attributable to granting the CO waiver to the entire industry. They found the variability in the rounding procedure to be more significant than the calculated effect of granting the waiver. If Ford had calculated the rollback modeling results to more significant figures, Ford estimates they would have found that air quality in 1985 would be at most 3.3 percent worse on a CO annual tonnage basis if the waiver is granted. (This 3.3 percent is the change in automobile contributions to total CO.) Ford calculates that an 8 grams/mile CO average in-field performance level would be necessary to achieve the CO air quality standard by 1990 in those areas where stationary sources alone do not exceed the standard (North Alaska). This can be compared to the 16.57 grams/mile CO average in-field performance level calculated by EPA to result from the 3.4 grams/mile LDV CO standard. Ford's projected in-field performance requirement neglects cold-start emissions, vehicle speed effects, and model accuracy.

Ford's feels that EPA's rollback model and associated data, as used in Reference 1, understate reductions in air pollution and that emission rates higher than 8 grams/mile average in-use performance figure may be adequate. Ford finds that fall and winter represent periods of higher CO concentrations than spring and summer. They also find that spring and fall represent the extremes in average CO concentrations but not the extremes in average temperature. For 1976 they calculated a correlation of CO air pollution with ambient temperature of −0.25 and conclude that there are other important factors besides temperature which influence ambient CO levels. Ford also presented data from a Chicago CAMP station near an eight lane arterial street which had seasonal CO pollution patterns which suggested what they considered to be a small seasonal effect on CO emissions. Ford did admit, however, that reasons for why greater CO pollution occurs in the fall or winter cannot adequately be explained by stationary source fossil fuel combustion.

Ford finds that air quality data show that significant improvement in CO levels in taking place. They also feel that, based upon this air quality data, EPA's model (from Reference 1) understates expected further reductions in CO air pollution.

b. Prediction of Future Urban Carbon Monoxide Concentrations. In this section of Ford's submission they discuss their own rollback model and compare the results that it predicts with those from various EPA models. Unfortunately this Ford work is dated (February 1975) and thus is not up to date and not comparable in either their results or data base to EPA's most recent (Reference 4) rollback work. Ford apparently made many different assumptions than EPA in deriving their model. Some of these differences include assuming no vehicular growth in the Central Business District and taking spatial distribution of emission sources into account. Ford claims validation of their rollback model based on its agreement with actual Los Angeles County CO data over the 1965 to 1972 time period. They also claim that their analysis demonstrates that greater weight should be given to the driving pattern in the urban centers where highest CO concentrations are observed. They suggest a revised driving cycle and different FTP weighting factors to increase the weighting of central business district driving.

This entire section (Attachment III of Ford's submission) is not pertinent as the work is out of date, the differences in their model versus EPA's are largely unspecified, the model validation is questionable in both its assumptions and breadth, and some of their suggestions and conclusions appear unsubstantiated.

c. The Vehicle Emissions Standard for CO and Air Quality. In this section Ford reiterates their position that the Federal Test Procedure (FTP) does not give a correct evaluation of the vehicle emissions responsible for the high CO concentrations observed in center-city locations. Ford claims that the FTP Bag 3 and particularly Bag 1 emissions are weighted too high in comparison to Bag 2 and that the use of these weightings overpredicts the effective CO emissions. Using this logic, Ford claims that a less stringent LDV CO emissions standard of 7.0 grams/mile, as measured on the FTP, is all that is needed as it does, in fact, correspond to a significantly lower effective CO emissions and thereby provides an additional margin of safety for the protection of public health. EPA studies indicates that catalyst equipped vehicles are probably in a "cold start" mode after a soak of only four hours. The EPA "hot spot" study indicates that high CO concentrations are not always a localized problem.(*8*)

d. Ford's Comments on Two EPA Documents. Ford commented on two EPA documents entitled "Air Quality Impact of Waiving the 3.4 Gram/Mile Automobile CO Standard" and "Status Report on the CO 'Hot Spot' Project." Both of these reports have been superseded by more recent analyses which are summarized elsewhere in this report. Many of Ford's criticisms have been rectified in the newer revisions of these reports which are discussed in this document.

e. Ambient Temperature Effect on Urban CO Air Quality. In this submission Ford has further discussed the sensitivity of CO air quality to the ambient temperature. Ford has modeled results of ambient CO measurements in both New York City and downtown Los Angeles. They have reported, as mentioned in an earlier section, that the dependence of CO concentrations on ambient temperature is weak. They also investigated with meteorological variables such as mixing height, wind speed and atmospheric stability might have an influence on CO concentrations. Ford found that by analysis of data from the 62 U.S. National Weather Service stations in the contiguous states from five year records that slowest dilution episodes occurred most frequently in December, followed in order by January, November, February, and October. This trend agrees well with observed seasonal patterns of 99th percentile CO values. Although Ford agrees that LDV CO emissions arise largely from vehicles in the cold start mode, they feel that their analysis shows that increased CO standards violations in the winter months can be primarily attributed to differences in meteorology.

5. Chrysler Corporation. Chrysler states that their position is that "The protection of public health does not require attainment of a 90 percent reduction for carbon monoxide (3.4 g/mi) by any of Chrysler's passenger car engine families in model years 1981 and 1982." They further state that " * * *.*. postponement of the 3.4 g/mi standard until 1983 would have no meaningful effect on overall air quality * * * ." Chrysler has divided their position into the following three arguments:

a. Health Effects of Carbon Monoxide. Chrysler feels that epidemiological studies have shown that there is no evidence of any relation between ambient CO levels and morbidity or mortality rates among the general public. They also feel that there is no evidence of significant CO-related cardiovascular problems within the sensitive population of angina patients although until a few years ago many cities were in almost daily violation of the present eight-hour CO NAAQS. They claim that the only documented CO health problems are those associated with actual poisoning or asphyxiation. There are a large number of CO health effect studies documented in EPA's CO Air Quality Criteria Document which contradict this view.

b. Ambient Air Quality and Automotive Emissions. Chrysler states that they feel that the present eight-hour CO NAAQS is sufficient to protect the public health and quote references who state that the present CO NAAQS should be protective of exercising individuals and that it represents an adequate safety margin. They also feel that the one-hour CO NAAQS is adequate.

Chrysler feels measured decreases in ambient CO levels are due to increasing numbers of controlled vehicles. They state that no violations of the one-hour CO NAAQS are presently being recorded and that the downtrend in eight-hour NAAQS violations is so strong that " * * * CO will be the first pollutant to come into compliance with its NAAQS." Chrysler references National Academy of Science, government, industry, and university computer modeling efforts which, they claim, show that a CO emission standard of 9 grams/mile would be adequate to meet the CO NAAQS. Chrysler claims to have used EPA's MOBILE1 model to show that granting of the CO waiver to the entire automobile industry "would slow overall improvement in air quality by only 10 weeks, and to Chrysler by only 11 days." They conclude: "The 'improvement' in air quality produced by going to 3.4 g/mi, whether in 1981 or 1983, must therefore be judged from any rational perspective as being completely negligible in its effects on the public health."

c. Computer Projections of Future Air Quality. Chrysler has interpreted and summarized the results of ten computer projections dealing with various automotive CO emission standards. These projections and Chrysler's interpretations are listed below:

(1) F.P. Grad, *et al;* "The Automobile and the Regulation of its Impact on the Environment" (1975): Chrysler summarizes this book as concluding: "Postponement of the 3.4 g/mi CO standard for five years would have little significant adverse consequences on total aggregate CO emissions in comparison to the reductions achieved since 1967. An interim standard of 9.0 g/mi of CO still results in a reduction of aggregate CO emissions at a rate of 14 percent per year. . . . (T)here is little ultimate difference between a 3.4 g/mi and a 7.0 g/mi standard. Each results in almost the same substantial yearly reduction in CO emissions. The effect of a two year waiver would be even slighter."

(2) 1975 Yale University Study (Partially funded by Chrysler Corporation) (1975): This study was an evaluation of the 1970 Clean Air Act to assess the adverse health effects of air pollutants emitted from automobiles and the expected benefits to be derived from automobile emission controls. The projections of the report suggested, according to Chrysler, that although reductions in automotive emissions are necessary for a substantial elimination of adverse health effects, the automotive emission standards need not be as stringent as the Clean Air Act requires. Their conclusion assumed that stationary sources would be controlled proportionally. By further comparison with several National Academy of Sciences studies, Chrysler was able to conclude that the Yale study showed that an automotive emissions standard of 9.0 or 15.0 grams/mile would be sufficiently stringent to achieve ambient CO concentrations which would prevent adverse health effects. The problem with this projection is that it predicts that an emission standard of 15 grams/mile would result in elimination of COHb levels and thus adverse health effects by 1981. As we approach 1981 this trend is not materializing.

(3) Denver Air Quality; Colorado Department of Health (1976, 77): The U.S. DOT has estimated that 99 percent of all CO emissions in Denver are vehicular in origin. Data from the Colorado Department of Health shows a year-by-year reduction since 1971 in the number of one- and eight-hour CO NAAQS violations. These reductions are attributed to reductions in vehicular emissions. The Colorado Board of Health projects 84 and 85 percent reductions in the one- and eight-hour CO standards respectively in Denver by 1975. The U.S. DOT projects no one-hour CO violations in Denver in 1985 and a 75 percent reduction over 1975 data of violations of the eight-hour standard. Chrysler claims that these trends "clearly indicate that present vehicle emissions regulations will bring an end to the CO problem in Colorado within the next few years. . . . " However, no mention is made in Chrysler's Summary as to which emission standards or factors were used for which years to make these projections.

(4) Panel on Air Quality, Noise, and Health, Interagency Task Force (1976): This report was prepared as a U.S. Government interagency effort to analyze the effects of various air pollution and noise emission limits on air quality, noise, and health implications through the year 2000. This report found that a 7.0 gram/mile LDV CO emission standard would result in a 80 to 85 percent average improvement in air quality from the base year (early

1970's) to the year 2000. Also, in the year 2000 no AQCR's were projected to be in violation of the CO NAAQS at a 9 grams/mile standard. The report also projected possible health consequences of various levels of emissions control for the years 1980, 1990, and 2000, as well as the period 1980 to 2000. They projected that a 15.0 grams/mile standard would be sufficient to reduce all excess cardiac deaths and disability to zero. Chrysler adds that a 7.0 grams/mile standard would thus provide "much more than adequate protection of the public health." Chrysler notes that this projection is based upon each standard being in effect for 23 years (1978–2000) rather than just two (1981–1982) as in the case of the CO waiver. This interagency report is considered to be somewhat dated. Many assumptions are made in the analysis that Chrysler does not detail. Some inspection/maintenance programs are assumed along with very low deterioration rates. EPA considers Reference 4 to be a more reliable source of information as it includes many updates and revisions.

(5) Future Urban Air Quality; Council on Environmental Quality (1977): In the Council on Environmental Quality's 1977 Annual Report, CO air quality projections were made. They found that with the exception of 16 urban areas, all cities are expected to meet the CO NAAQS by 1985. The 16 cities are also expected to be in compliance by 1990. These calculations are based on rollback modeling using 15 grams/mile as an average, on-the-road automobile emission rate for 1990. Chrysler fails to point out that an average, on-the-road, emission value of 15 grams/mile actually represents a much lower emission standard because in-use deterioration is much greater than is predicted under certification type conditions.

(6) Automotive Air Pollution; National Academy of Sciences (1977): Chrysler quotes several sections of the NAS report entitled "Implications of Environmental Regulations for Energy Production and Consumption." The first comment states that CO related health problems are important only to people spending many hours in areas of heavy traffic congestion and that the CO health benefits from a stringent auto emissions standards are minimal compared to those to be gained from CO from cigarette smoke and home gas-fired heaters. The second comment states that "carbon monoxide is not deemed a significant hazard to today's community health at today's (15 grams/mile) emission levels; although the cost of meeting a more stringent standard of carbon monoxide seems low, the added benefits to community health are questionable and the resulting compromise with hydrocarbon elimination should be avoided."

(7) Revised Weighting of CVS/CH Test for CO Emissions; Ford Motor Company (1978): Chrysler, in this section, mentions Ford's contentions that FTP CO emissions are not representative of those found in urban rush hour traffic. They suggest Bag 2 emissions as more appropriate. Ford feels that with the present FTP conditions, a CO emission standard of 11–12 grams/mile would be sufficient to meet the CO NAAQS. Again, in this section Chrysler gives insufficient data or analyses to make use of their projection. EPA's "Hot Spot" report gives some indication that CO may be a regional problem.

(8) Air Quality Impact of Waiving the 3.4 gram/mile Automotive CO Standard; EPA (1978): A revision of this EPA report has been reviewed in the first section of this report.

(9) Effect of a Two-Year Delay on Total Emissions; John B. Pierce Foundation Laboratory (No date): Chrysler hired the John B. Pierce Foundation Laboratory of Yale University to verify its calculations of the effect of a two-year delay in the imposition of the 1980–81 automotive emission standards on Chrysler cars. Calculations showed that holding the CO standard at 15 grams/mile for 1980 and 1981 Chrysler would, for the 1980–1990 time frame, increase CO emissions by a ratio of 1.0086:1. This represents a six week delay in the attainment of air quality benefits. Chrysler feels that: "* * * Holding at 15 grams/mile for two more years is twice as severe a case as holding at 7 grams/mile instead of 3.4 grams/mile for 1981–82. Nevertheless, delay in the expected decrease of total emissions would be only six weeks. The effect on air quality of public health would be so small as to escape detection with any current methodology."

(10) Chrysler's Application of EPA's MOBILE1: Mobile Source Emissions Model: Chrysler reports in this section on their use of and projections made with EPA's MOBILE1 model. The emission factors and methodology used are those described in EPA's "Mobile Source Emission Factors, Final Document." Chrysler has modified the program to allow various timetables for emission standard implementation. Chrysler chose to look at the effects of a CO waiver on air quality in New York and Colorado (as "worst-case" examples), as well as on a national basis. Chrysler found for 1987, the year of maximum air qualify effect, a 2.0 percent difference in CO emissions from all manufacturers' vehicles resulted between the waiver and non-waiver scenarios on a nationwide basis. For New York and Colorado the maximum percent differences were 2.7 and 2.1 percent respectively. For a Chrysler only waiver (assuming a 15 percent market share for Chrysler) the maximum nationwide difference in vehicle emissions found to be 0.30 percent while the New York and Colorado differences were 0.40 and 0.32 percent, respectively. Chrysler states that this shows that a two-year waiver would thus have no practical effect on CO emissions or on air quality and public health. They further state that "* * * if a two year waiver to 7.0 grams/mile were granted to the entire industry, the resulting delay in reduction of CO emissions would slow the rate of improvement in air quality by only 10 weeks. If the waiver were granted to Chrysler alone, the rate of improvement in air quality would be slowed by a mere 11 days. It is difficult to believe that air monitoring stations could even detect this difference."

References

(1) Memo from Edward J. Lillis, Chief, Air Management Technology Branch to Michael P. Walsh, Acting DAA, Office of Mobile Source Air Pollution Control, "Air Quality Impact of Waiving the 3.4 g/m Automotive CO Standard," July 18, 1978.

(2) Memo from Edward J. Lillis to Michael P. Walsh, "Revised Air Quality Projections for Waiving the 3.4 g/m Automotive CO Standard," August 11, 1978.

(3) Memo from Edward J. Lillis to Charles L. Gray, Director, Emission Control Technology Division, "Air Quality Analysis of Waiving the 3.4 Gram/Mile CO Standard for Light-Duty Vehicles," May 14, 1979.

(4) "Revised Air Quality Analysis of Waiving the 3.4 Gram-Mile CO Standard for Light-Duty Vehicles," EPA, August, 1979.

(5) Memo from Charles L. Gray, Director, ECTD to Robert E. Neligan, MDAD, "OAQPS Support on CO Waiver Requests Under Section 202(b)(5)(a) of the CAA," March 9, 1979.

(6) U.S. DOT, EPA, and Federal Energy Administration, "An Analysis of Alternative Motor Vehicle Emission Standards," May 19, 1977.

(7) U.S. Environmental Protection Agency, "Mobile Source Emission Factors, Final Document," EPA–400/9–78–006, March 1978.

(8) Shelar, E., F. L. Ludwig, and H. Shigeishi, Atmospheric Science Center, SRI International for the U.S. Environmental Protection Agency, "Analysis of Pollutant and Meteorological Data Collected in the Vicinity of Carbon Monoxide 'Hot Spots,' " Discussion Draft, May 1979.

(9) U.S. Environmental Protection Agency, "Motor Vehicle Tampering Survey (1978)," November 1978.

(10) Additional Submission for CO Waiver Docket from Betsy Anchor-Johnson, Vice-President, GM Environmental Activities Staff, to Benjamin R. Jackson, DAA, EPA Mobile Source Noise and Enforcement, dated July 20, 1979.

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Part III

Environmental Protection Agency

Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[FRL 1323-D]

Guidelines Establishing Test Procedures for the Analysis of Pollutants

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed regulation.

SUMMARY: EPA proposes to amend its list of approved analytical techniques by adding test procedures for 113 organic toxic pollutants, an additional test procedure for inorganic toxic pollutants, a procedure for carbonaceous BOD_5, and requirements for sample preservation and holding times. The use of these procedures would be required for filing applications for National Pollutant Discharge Elimination System (NPDES) permits, for State certifications, and for compliance monitoring under the Clean Water Act. After considering comments received in response to this proposal, EPA will promulgate a final rule.

DATES: Comments on this proposal must be submitted on or before February 1, 1980.

ADDRESS: Send comments to Dr. Robert B. Medz, Monitoring Technology Division, Office of Research and Development, Environmental Protection Agency (RD-680), 401 M Street, S.W., Washington, D.C. 20460.

FOR FURTHER INFORMATION CONTACT: Dr. Robert B. Medz at the address listed above or call (202) 426-4727.

SUPPLEMENTARY INFORMATION:

I. Authority and Background

This regulation is proposed under authority of sections 304(h) and 501(a) of the Clean Water Act, 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) (the "Act"). Section 304(h) of the Act requires the Administrator of the EPA 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 this Act or permit application pursuant to section 402 of this Act." Section 501(a) of the Act authorizes the Administrator to "prescribe such regulations as are necessary to carry out his functions under this Act."

EPA promulgated "Guidelines Establishing Test Procedures for the Analysis of Pollutants" in 40 CFR Part 136 on October 16, 1973 (38 FR 28758). These guidelines, which were amended on December 1, 1976 (41 FR 52780), provided test procedures for 115 well known pollutants and pollutant parameters, including metals and a number of organic compounds. The guidelines also provided "recommendations" for sample preservation techniques and holding times. Only when these preservation techniques and holding times were stipulated in the analytical methods description were they regarded to be mandatory.

Since publication of those guidelines, EPA entered into a Settlement Agreement requiring it to study, if necessary, regulate 65 "priority" pollutants and classes of pollutants. (*See Natural Resources Defense Council, Inc., et al v Train,* 8 ERC 2120 (D.D.C. 1976), modified 12 ERC 1833 (D.D.C. 1979)). In December 1977, Congress passed the Clean Water Act of 1977, emphasizing the control of toxic pollutants and declaring the 65 "priority" pollutants and classes of pollutants to be "toxic" under section 307(a) of the Act.

The list of 65 toxic pollutants and classes of pollutants potentially included thousands of substances, many of which were relatively unknown outside the scientific community; moreover, because only on rare occasions had industry monitored for or had EPA regulated these pollutants, section 304(h) analytical methods were not available in many cases. In order to implement the Act, therefore, EPA first streamlined its regulatory task by defining 129 specific toxic pollutants for initial consideration. Next, the Agency embarked on an intensive literature search and laboratory program to develop section 304(h) methods for these 129 toxic pollutants.

This proposed amendment to 40 CFR Part 136 will provide analytical methods for 113 organic toxic pollutants. For each of these pollutants, two acceptable methods are proposed: (1) Either gas chromatography (GC) with selected detectors, or high performance liquid chromatography (HPLC), depending on the particular pollutant; and (2) GC coupled with mass spectrometry (GC/MS). This proposed amendment also provides another option for analysis of inorganic toxic pollutants by inductively coupled plasma optical emission spectoscopy (ICP), which may be less time-consuming and costly than existing section 304(h) methods for inorganics. Additionally, this proposal provides sample preservation and maximum holding times for a large number of pollutants covered by these proposed or existing section 304(h) methods. Finally, a method for analysis of carbonaceous BOD_5 is included in this proposal.

The use of these testing procedures would be mandatory whenever the measurement of waste constituents is required under the Clean Water Act. For example, on June 14, 1979, EPA published a Draft Consolidated Permit Application Form and Proposed NPDES Regulations, which would require that certain applicants for NPDES permits analyze their discharges for the 129 specific toxic pollutants (See 44 FR 34346). The use of these procedures also would be required for section 401 State certifications under 40 CFR Part 121 and for NPDES compliance monitoring under 40 CFR Part 122 (See 44 FR 32854, June 7, 1979). Additionally, in accordance with 40 CFR 401.13, these testing procedures would apply to expression of pollutant amounts in effluent limitations guidelines, standards of performance, and pretreatment standards (including any monitoring requirements contained therein) under 40 CFR Part 402 et seq., "unless otherwise specifically noted or defined in said parts."

II. Summary of Proposed Methods

A. GC and HPLC Methods

A series of 12 new test procedures are being proposed that employ conventional GC or liquid chromatographic techniques for the quantitative measurement of specific organic materials. Although these methods can sometimes be used for qualitative identification of unknown materials in a sample, they are best used for the measurement of materials that are already known to be present in the sample. The low cost of the conventional detectors relative to MS makes this approach particularly attractive for routine monitoring of expected concentration levels of pollutants. HPLC has developed considerably in the past few years and can be used to achieve separations and measurements that cannot be performed with state-of-the-art GC.

These 12 methods numbered 601 to 612 were developed through in-house and contracted research through EPA's Environmental Monitoring and Support Laboratory, Cincinnati (EMSL-Cin). The 114 organic compounds for which analytical procedures were needed were divided into 12 categories based on their chemical structure in the expectation that members of each class might be analyzed by a single procedure or perhaps with minor variations on a single basic procedure. Separate requests for proposals were issued for each class and, after competitive bidding, contracts were awarded to a total of five laboratories. Each research effort concentrated on the development of a test procedure with good sensitivity and reliability with full consideration of economic factors including: (1) Availability of instrumentation required; (2) availability of trained personnel capable of performing the analyses; (3) commercial availability, cost and reliability of additional peripheral equipment such as specific detectors and new types of column packings. The 12 methods that resulted from this effort represent state-of-the-art analytical technology.

Methods 601 and 603 are for the measurement of solvents and other volatile materials using variations of the Bellar purge and trap technique. Semispecific detectors are used to minimize background interferences. Seven of the methods involve solvent extraction techniques followed by conventional GC measurements. Cleanup procedures are included with these methods to overcome interferences. Method 605 for benzidines, and Method 610 for polynuclear aromatic hydrocarbons (PAH), rely on HPLC techniques for separation and measurement, although GC is acceptable for use in the measurement of most of the PAH materials.

Each method has been evaluated by the contractor for applicability to a variety of industrial and municipal effluents and each has provided acceptable levels of sensitivity, accuracy, and precision. The Agency is conducting interlaboratory accuracy and precision studies for these 12 methods and will make the results available as soon as these studies are completed.

A copy of the full text of these methods is included as Appendix I to this preamble for the convenience of the public who desire to review it and make comments.

B. GC/MS Methods

Three new test procedures, 613, 624, and 625, are being proposed that require a mass spectrometer detector. Although historically used as a qualitative tool by the analytical chemist, the development of stable electronics and advanced software has resulted in the widespread use of the GC/MS system to quantitate pollutant levels in environmental samples. Although the capital investment for the instrumentation is relatively high, the instrument allows for the simultaneous measurement of large numbers of materials. In addition, the detector can be used to overcome interferences that would mask compound responses obtained with less specific GC detectors. Because of these potential economic advantages to the user, EPA has decided to propose both GC/MS and non-MS approaches so that the user may select the most cost-effective one to suit his monitoring requirements.

Method 613 for Tetrachlorodibenzodioxin (TCDD) was developed through one of the series of EPA contracts discussed above. It involves the use GC/MS to measure low quantities of TCDD after solvent extraction and extensive cleanup of the extract.

Methods 624 and 625 were developed by the combined efforts of the EMSL-Cin and of the Environmental Research Laboratory (ERL), Athens, Georgia. Methods 624 and 625 essentially represent the techniques described in *Sampling Procedures for Screening Industrial Effluents for Priority Pollutants (April 1977).* These methods have been used extensively by EPA's Effluent Guidelines Division (EGD), Regional laboratories and contractors, and by many private laboratories.

A copy of the full text of these methods is included as Appendix II to this preamble for the convenience of the public who desire to review it and make comments.

The Agency is reviewing a number of approaches, involving the analyses of a wide variety of sample types, to determine more thoroughly the precision and accuracy of these techniques. The Agency is considering, also, the addition of more extensive quality assurance and quality control proceedings for proposed methods 624 and 625. The approaches include the potential use of internal standards, surrogate spikes, and labeled compounds. Appendix III to this preamble provides an example of such an additional quality assurance program for public review and comment.

C. Elemental Analysis

The Agency is proposing an ICP method for elemental analysis of the toxic metals. This technique, which is an alternative to existing 304(h) methods for metals, provides a simultaneous multi-element determination of trace elements in solution. Dissolved elements are determined in filtered and acidified samples. Total elements are determined after appropriate digestion procedures are performed. The basis of this instrumental method is the measurement of atomic emission by an optical spectroscopic technique.

The Agency developed the proposed method by requesting the ICP Users Group, consisting of EPA personnel that presently have various makes and models of satisfactory instruments, to provide their input into a methods write-up to be prepared by the staff of the EMSL-Cin. The resulting method represents the current state-of-the-art. The EGD also has made extensive use of ICP procedure. It has already been approved for use in the NPDES permits system on a Regional basis. Improvements are anticipated as time progresses. Users are encouraged to identify problem areas and assist in updating the method.

The write-up includes a list of the elements for which the method applies along with recommended wavelengths and typical estimated instrumental detection limits. Because of the differences between satisfactory instruments, no detailed instrumental operating conditions are provided. Instead, the analyst is referred to the instructions provided by the manufacturer of the particular instrument. Potential matrix interferences are given and instructions for appropriate corrections are provided.

EPA is planning to conduct an interlaboratory precision and accuracy study, using a wide variety of treated effluent samples, to evaluate potential matrix interferences. The Agency will make these studies available as soon as they are completed.

A copy of the full text of the ICP procedure is included as Appendix IV to this preamble for the convenience of the public who desire to review it and make comments.

D. *BOD_5* Carbonaceous Method

This method of carbonaceous BOD has been provided in response to many requests for this parameter. It measures the carbonaceous BOD of a sample with the currently approved procedure after first adding a reagent to act as a nitrogen oxygen demand suppressant. A copy of the full text of the BOD_5 method is included as Appendix V to the preamble for the convenience of the public who desire to review it and make comments.

E. Requirements for Sample Containers, Preservation Procedures and Holding Times

Several commentators on the June 9, 1975 Proposed Amendments to the Guidelines Establishing Test Procedures for the Analysis of Pollutants (40 CFR Part 136) requested criteria for sample preservation and holding times. As a result, on December 1, 1976, the Agency cited the recommendations given in "Methods for Chemical Analysis of Water and Wastes," U.S. Environmental Protection Agency, Table II, pp. VIII–XI, 1974, as applicable to the NPDES samples.

Since December 1976, there have been many requests for clarification as to whether the preservation procedures and holding times were recommendations or requirements for NPDES monitoring. Several laboratories also commented that the holding time recommendations were difficult and very expensive to follow because of the short time interval allowed between sample collection and analysis for many of the common parameters.

It is the proposal of the Agency that the sample preservation procedures and holding times published be requirements and not just recommendations. However, the guidance given in the reference cited above was intended for broad application to all environmental sample types. The Agency realizes that it might be less applicable to require laboratories to use preservation procedures and holding times for general uses which extended beyond NPDES monitoring. the Drinking Water Program, for example, has addressed this problem and requires procedures specifically designed for drinking water samples. These have been published in the "Manual for the Interim Certification of Laboratories Involved in Analyzing Public Drinking Water Supplies—Criteria and Procedures," USEPA, Report No. EPA 600/8–78–008, May 1978.

Data collected by the Agency, data in the scientific literature, and data submitted to the Agency by public and private laboratories have been reviewed to determine the state-of-the-art as it applies specifically to the preservation of NPDES samples. The criteria used in reviewing the data and selecting sample preservation procedures and maximum holding times were: (1) That the procedures would retard significant sample degradation, and (2) that the procedures would minimize monitoring costs by extending the holding times when possible.

A list of requirements for sample containers, preservation procedures and maximum holding times for NPDES monitoring is proposed in § 136.3(d), Table II. Information given in § 136.3(d), Table II supersedes past recommendations and directions given by the methods listed in the manuals and references cited in § 136.3(a), Table I.

The preservation procedures listed in Table II are to be used at the start of sample collection in the field and not after sample compositing is completed or when the samples are received in the laboratory for analysis. Aliquots of composite samples, which would require multiple preservatives, should be preserved only by maintaining at 4°C until compositing and sample splitting are completed.

The holding times listed in Table II are the maximum times between sample collection and analysis that are allowed for the sample to be considered valid. When possible, all laboratories are encouraged to analyze samples as quickly as possible after collection. The data base available to EPA shows that no more than 10% sample deterioration occurs when samples are preserved as prescribed in Table II and held for the maximum holding time.

Some effluent samples may be stable longer than the maximum holding time for a given parameter. A longer holding time may be used as long as the discharger or monitoring laboratory has data on file showing the validity of the longer time. Also, some samples may not be stable for the maximum time period given in the table. A discharger or monitoring laboratory is obligated to hold the samples for a shorter time if knowledge exists to show this is necessary to maintain sample stability.

The Agency believes that the proposed requirements for sample preservation will save the monitoring community a substantial savings over the next several years. The recommendations for sample preservation cited in 40 CFR Part 136, December 1, 1976, list holding times of only 24 hours for many common parameters. Many monitoring organizations meet these short holding times by locating small "field," "Regional," or "district" laboratories close to the points of sample collection to minimize travel time. Other organizations maintain large centralized laboratories, ship samples by express methods and work overtime to meet the short holding times. Both of these approaches are very expensive. The proposed extended holding times requirement will allow organizations to review the need for small "field" laboratories, and institute more economical methods of sample shipment and analysis.

III. Cost and Economic Impacts

This proposed regulation does not require monitoring and therefore, does not directly impose costs on the monitoring community. Use of the analytical methods proposed, however, may be required in a variety of EPA programs. Because the costs of analyses may constitute a significant fraction of the cost for some programs, EPA will adress overall economic impacts in program-specific regulation (e.g., economic discussions concerning the recently published Draft Consolidated Permit Application Forms and Proposed NPDES Regulations, starting at 44 FR 34408, June 14, 1979). Nevertheless, the Agency is interested in the unit cost for various analyses since they may be needed to assess the impact of alternative approaches to a given program.

A. Carbonaceous BOD_5

No significant incremental cost is expected for the Carbonaceous BOD_5 method proposed today relative to the previously promulgated BOD_5 method (which measures both carbonaceous and nitrogenous oxygen demand). The main difference between these methods is the use in the Carbonaceous BOD_5 test of an additional chemical to inhibit nitrogenous oxygen demand. Previous estimates of the cost to perform a BOD_5 test on 10–20 samples ranged from $15–$30 per sample.

B. Maximum Holding Times

In the past, maximum sample holding times prior to completion of analysis were not standardized. Small "field," "regional," or "district" EPA, State, commercial and industrial laboratories needed to be close to the source of samples so that the samples could be analyzed quickly after collection. This presented an obstacle to the management trend for more efficient use of equipment and personnel by centralizing laboratory operations. Because of the lack of standardization, incremental costs between past practices and the maximum holding times proposed today cannot be accurately estimated by the EPA. However, the EPA believes that the proposed requirements for sample preservation could save the monitoring community substantial savings. Short sample holding times for many parameters which resulted in increased operational costs would be removed by approval of these proposed requirements. It should be noted that the impact on on-site plant laboratories will be slight.

C. GC and HPLC Methods

EPA has obtained preliminary cost estimates for performance of serveral methods proposed today. It was assumed that properly preserved but unextracted industrial effluent samples were delivered to the laboratory and that a typical lot might involve 40–50 repetitions of a given analytical method. The highest estimate for performance of a given method was typically 3 to 4 times the lowest. Average figures are presented in the following table.

A cost estimate for Method 613 which involves use of GC/MS is included in this table due to the specific focus of this method on dioxin (in contrast to the broader focus of Methods 624 and 625). Estimates are not yet available for Methods 606 and 607. The Agency is continuing to gather data on all methods to better characterize these costs.

Method No.	Method name	[1] Average
601	Purgeable Halocarbons	130
602	Purgeable Aromatics	150
603	Acrolein/Acrylonitrile	110
604	Phenols	200
605	Benzidines	220
606	Phthalate Esters	110
607	Nitrosamines	150
608	Organochlorine Pesticides & PCBs	110
609	Nitroaromatics and Isophorone	210
610	Polynuclear Aromatic Hydrocarbons	310
611	Haloethers	120
612	Chlorinated Hydrocarbons	160
613	2,3,7,8-Tetrachlorodibenzo-p-dioxin	170

[1] Average estimated cost (dollars per method, per sample).

D. GC/MS Methods

The cost of analyzing the 113 organic toxic pollutants by the GC/MS Methods proposed today has been estimated at a range of $1,000 to $2,000 for quantitative analysis depending upon the amount of quality assurance required. The assumptions and basis for these figures were discussed at length at 44 FR 34408, June 14, 1979.

E. ICP Method

The agency has not yet completed a survey of the unit cost for ICP analysis for metals, but much of the interest in this method stems from its ability to simultaneously analyze for many metals. Analysis for the same series of metals may be performed (one at a time) using atomic adsorption (AA) spectroscopic methods promulgated earlier (41 FR 52780, December 1, 1976).

Since the sensitivity of ICP is generally similar to AA methods, the recent widespread interest in ICP suggests that the cost per pollutant analyzed may be lower with ICP than with AA. The contract cost per pollutant for 10–20 samples using AA typically averages $10.

IV. Future Rulemaking

The following areas of concern are under consideration by the EPA for amendment of the proposed section 304(h) regulation in the near future:

A. Methods for Measuring the Acute Toxicity of Effluents to Aquatic Organisms (Biomonitoring)

Biomonitoring methods are intended for use in determining whether a waste water stream is significantly toxic. These biomonitoring methods may become required measurements in support of the Consolidated Permits Application Regulation which was developed by the Office of Enforcement.

B. Procedures for Determining Detection Limits in Support of the Proposed Consolidated Permit Application Form

In the proposed consolidated regulation, EPA may establish pollutant limitations based upon reported levels in the waste water or a multiple of the detection limit of the analytical method if the pollutant is not detected.

C. An Analytical Procedure to Measure Asbestos in Water

The Agency has already developed an interim method which is being tested for asbestos by environmental analysis laboratories. The present method defines the presence of both chrysotile and amphiboles, but chrysotile is more readily identified. Incoming data from the laboratories is being intercompared in order to improve definition of asbestos fibers and determine the precision, accuracy, and percent recovery of the method in waste water.

D. Updating the Reference in 40 CFR Part 136

Many of the references cited in 40 CFR Part 136 have been superseded by later editions. EPA is planning to amend the regulation to include the following references:

1. "Methods for Chemical Analysis of Water and Wastes, 1979," U.S. Environmental Protection Agency, EPA–600/4–79/020.
2. "Annual Book of Standards, 1979," American Society for Testing Materials, Part 31, Water.
3. "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 unless otherwise stated.

E. Additional Procedures for the Analysis of Organic Pollutants in Wastewater

EPA is planning to propose two additional analytical methods applicable only to specific organic chemicals Standard Industrial Classification (SIC) codes. The first method consists of the GC/MS procedures proposed today, together with the addition of several deuterated internal standards and/or isotopically labeled compounds. The second procedure consists of variations of the GC procedure currently being proposed which are specific to the wastewater matrix found in a specific organic chemical industry (by SIC codes).

F. Development of an EPA Policy on Mandated Control of the Usage of Known or Suspected Carcinogenic Reagents

The Agency shall consider the development of a policy on the usage of known or suspected carcinogenic reagents in environmental analysis. A determination shall be made as to whether the EPA should approve the use of such reagents when other, noncarcinogenic, acceptable reagents are available. Consideration shall be given to the establishment of control of the disposal of known or suspected carcinogenic reagents in order to prevent their introduction to the environment.

V. Request for Comments

A. GC, GC/MS, HPLC

1. EPA solicits comments on the general applicability of the proposed GC, GC/MS, and HPLC methods, or other methods which have been used for measuring "toxic" pollutants in industrial discharges. The Agency is particularly interested in comments on interferants and other analytical obstacles which have been experienced and how these obstacles were overcome to allow quantitative estimations to be made.

2. Commentators are urged to make any data which they may have to better define the sensitivity, precision, accuracy, and detection limits of the proposed methods available to the Agency.

3. Several different configurations of GC columns, detectors, and operating conditions have been indicated in the proposed methods. Comments are solicited on the optimum flexibility which should be specified in such configurations in tailoring the GC, GC/MS, and HPLC procedures for their most general applicability to industrial discharges.

4. The proposed methods have included a minimum level of quality control, that is, the use of replicates, spikes, and blanks as necessary operations. EPA solicits comments regarding the additional levels of quality control that should be specified in the procedures, if any, and those elements of quality control which should be left to the analyst's discretion. Earlier, in the preamble, a suggested intensive quality control regime was discussed which could be included in the GC/MS methods. Comments are solicited relative to the adequacy and desirability for integrating much more intensive quality control requirements within the mandatory language of the GC/MS methods.

5. The proposed regulation includes mandatory preservation techniques and maximum holding times based upon data accumulated by EPA since 1975. The Agency seeks additional data and comments concerning preservation techniques and maximum holding times.

6. EPA is proposing an ICP instrument to supplement the present colorimetric and AA procedures. The Agency believes that the proposed ICP procedures should provide greater flexibility to the analyst to choose the most appropriate analytical technique for measurement of trace elements. Comments are solicited especially relative to the general applicability of ICP to industrial discharges.

7. In response to requests from environmental analysis laboratories that desire to measure the carbonaceous BOD of municipal and industrial wastewaters without the complications caused by the nitrogenous oxygen demand, the carbonaceous BOD method is being proposed. The nitrificaton control incorporated in the proposed method offers an analytical advantage in greatly improving the reproducibility of BOD measurements. The advantages offered by the proposed method's ability to distinguish between carbonaceous and nitrogenous oxygen demands are expected to favorably impact the design and operation of biological nitrification plants because loadings, aeration rates, and chemical doses are based largely on the nitrogenous demand. EPA requests additional data on the control of nitrification in BOD measurements.

8. EPA's cost estimates for the proposed methods are based upon all available data. The Agency solicits comments and data on the estimated unit cost of the proposed methods. Commentators should state the assumptions underlying their estimates.

Dated: November 16, 1979.

Barbara Blum,

Acting Administrator.

Appendices

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Appendix I: Gas Chromatographic and HPCL Methods—Methods 601 through 612.

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Appendix V: Biological Oxygen Demand Carbonaceous Method 405.1 (5 days, 20° C).

Appendix I—Gas Chromatographic and HPLC Methods—Methods 601 through 612

Purgeable Halocarbons—Method 601

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.*
Bromoform	32104
Bromodichloromethane	32101
Bromomethane	34413
Carbon tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34105
1,2-Dichlorobenzene	34536
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
Dichlorodifluoromethane	34668
1,1-Dichloroethane	34496
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachloroethene	34475
1,1,1-Trichloroethane	34506
1,1,/2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34488
Vinyl chloride	39175

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed purging chamber. The halocarbons are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a short sorbent tube where the halocarbons are trapped. After the purge is completed, the trap is heated and backflushed with gas to desorb the halocarbons into a gas chromatographic system. A temperature program is used in the GC system to separate the halocarbons before detection with a halide-specific detector.

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing 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 method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free 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 soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1. Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

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

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Several complete devices are now available commercially. The device must meet the following specifications: The unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in Figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including halide-specific detector, column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 μl.

4.6 2-way syringe valve with Luer ends (3 each).

4.7 Syringe—5-ml gas-tight with shut-off valve.

4.8 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Regents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porus polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.2 Three percent OV-1 on Chromosorb-W 60/80 mesh.

5.2.3. Silica gel—(35/60 mesh)—Davison, grade-15 or equivalent.

5.2.4 Coconut charcoal 6/10 mesh Barnaby Chaney, CA-580-26 lot # M-2649 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge ahd trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of

5.4.2 A water purfication system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle and seal with a Teflon line septum and cap.

5.5 Stock standards—Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders 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.

5.5.1 Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—Using a 100 μl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards for any of the six halocarbons that boil below 30° C (bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorodifluoromethane, 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 methyl alcohol menicus. Slowly inject the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards weekly for the six gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standard each month.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The standards shoud be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the analytical system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of standard in methyl alcohol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 8. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978) before reliable sample analysis may begin.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of 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 blank with surrogate halocarbons. A combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane is recommended to encompass the boiling range covered by this method. From stock standard solutions prepared as above, add a volume to give 1000 μg of each surrogate to 45 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume (20 ng/μl). Dose 5.0 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.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume in excess of 40 ml. Fill the sample bottles 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.

8.2. The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 14 days of collection.

9. *Sample Extraction and Gas Chromatograph.*

9.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the samples 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 5.0 ul of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.3 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.

9.4 Close both valves and purge the sample for 11.0 ± .05 minutes.

9.5 After the 11 minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while back-flushing the trap with an inert gas between 20 and 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or sub/ambient, if problems persist) instead of the initial program temperature of 45°C.

9.6 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 organic-free water.

9.7 After desorbing the sample for approximately four minutes recondition the trap by returning the purge and trap device 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 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.

9.8 Table 1 summarizes some recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by column 1 is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentration levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (μg/l) vs. peak height or area units.

10.2 Reports results in micrograms per liter. When duplicate and spiked samples are samples are analyzed, all data obtained should be reported.

11. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an inter-laboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, Vol. 66, No. 12, Dec. 1974, pp. 739–744.

2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Proceeding from ASTM Symposium on Measurement of Organic Pollutants in Water and Wastewater, June 1978 (In Press).

3. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11—Purgeables and Category 12—Acrolein, Acrylonitrile, and Dichlorodifluoromethane." Report for EPA Contract 68–03–2635 (In preparation).

Table 1—*Organohalides Tested Using Purge and Trap Method*

Compound	Retention time (min.)		Detection limit[1]
	Col.1[2]	Col. 2[3]	μg/l
Chloromethane	1.50	5.28	0.0009
Bromomethane	2.17	7.05	0.03
Dichlorodifluoromethane	2.62	(4)	0.03
Vinyl chloride	2.67	5.28	0.01
Chloroethane	3.33	8.68	0.01
Methylene chloride	5.25	10.1	0.01
Trichlorofluoromethane	7.18	(4)	0.01
1,1-Dichloroethene	7.93	7.72	0.006
1,1-Dichloroethane	9.30	12.6	0.004
trans-1, 2-Dichloroethene	10.1	9.38	0.006
Chloroform	10.7	12.1	0.006
1,2-Dichloroethane	11.4	15.4	0.006
1,1,1-Trichloroethane	12.6	13.1	0.005
Carbon tetrachloride	13.0	14.4	0.007
Bromodichloromethane	13.7	14.6	0.006
1,2-Dichloropropane	14.9	16.6	0.004
trans-1,3,-Dichloropropene	15.2	16.6	0.006
Trichloroethene	15.8	13.1	0.005
Dibromochloromethane	16.5	16.6	0.01
1,1,2-Trichloroethane	16.5	18.1	0.006
Cis-1,3-dichloropropene	16.5	18.0	0.008
2-Chloroethylvinyl ether	18.0	(4)	0.06
Bromoform	19.2	19.2	0.02
1,1,2,2-Tetrachloroethane	21.6	(4)	0.006
Tetrachloroethene	21.7	15.0	0.007
Chlorobenzene	24.2	18.8	0.03
1,3-Dichlorobenzene	34.0	22.4	0.04
1,2-Dichlorobenzene	34.9	23.5	0.04
1,4-Dichlorobenzene	35.4	22.3	0.04

[1] Detection limit is calculated from the minimum detectable GC response being equal to five time the GC background noise, using a Hall Model 700-A Detector.

[2] Carbopack B 60/80 mesh coated with 1% SP-1000 packed in an 8 ft × 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° then held for 15 min.

[3] Porisil-C 100/120 mesh coated with n-octane packed in a 6 ft × 0.1 in ID stainless steel or glass column with helium carrier gas at 40 ml/min flow rate. Column termperature held at 50°C for 3 min then programmed at 6°C/min to 170° then held for 4 min.

[4] Not determined.

BILLING CODE 6560-01-M

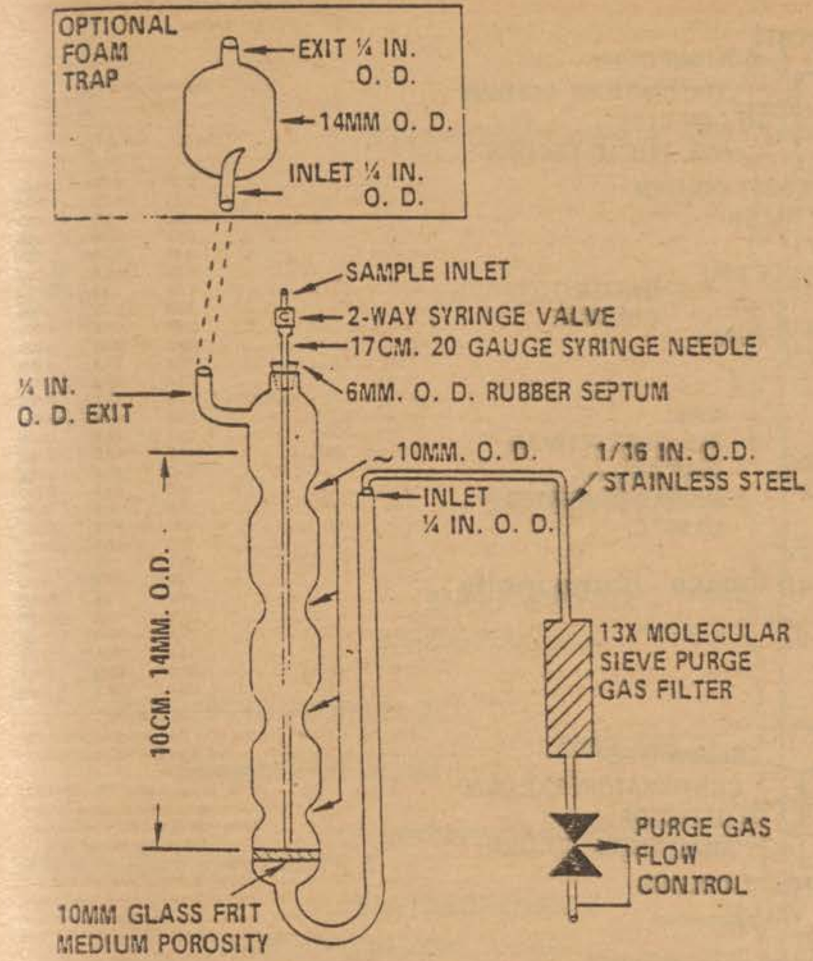

Figure 1. Purging device

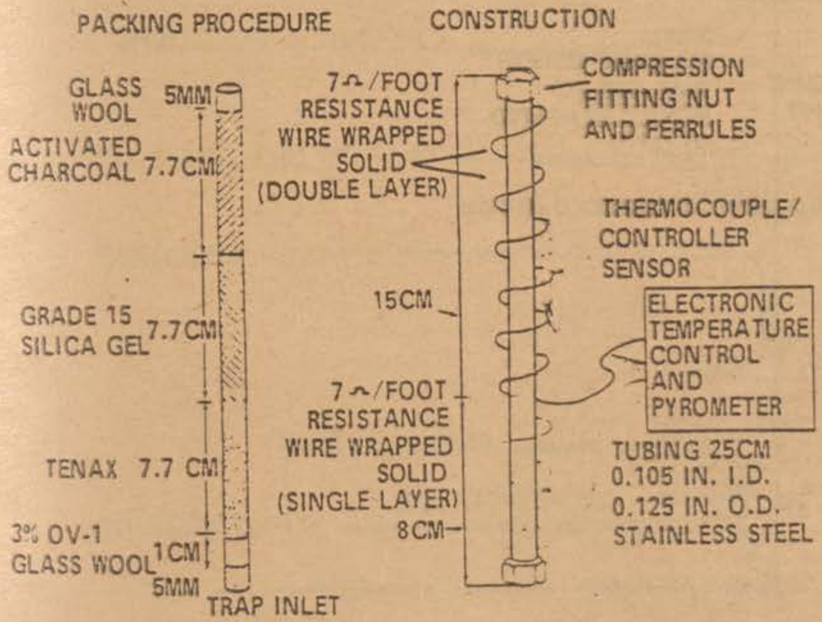

Figure 2. Trap packings and construction to include desorb capability

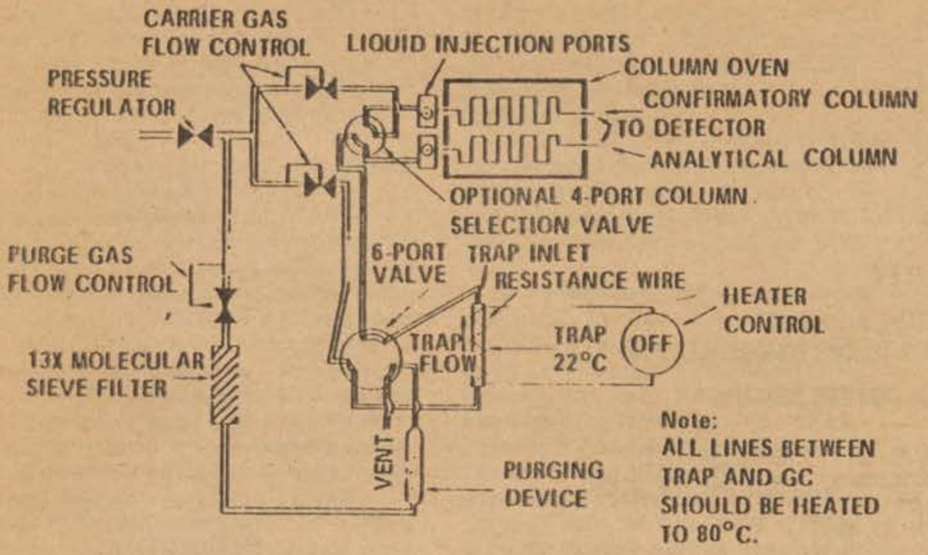

Figure 3. Schematic of purge and trap device - purge mode

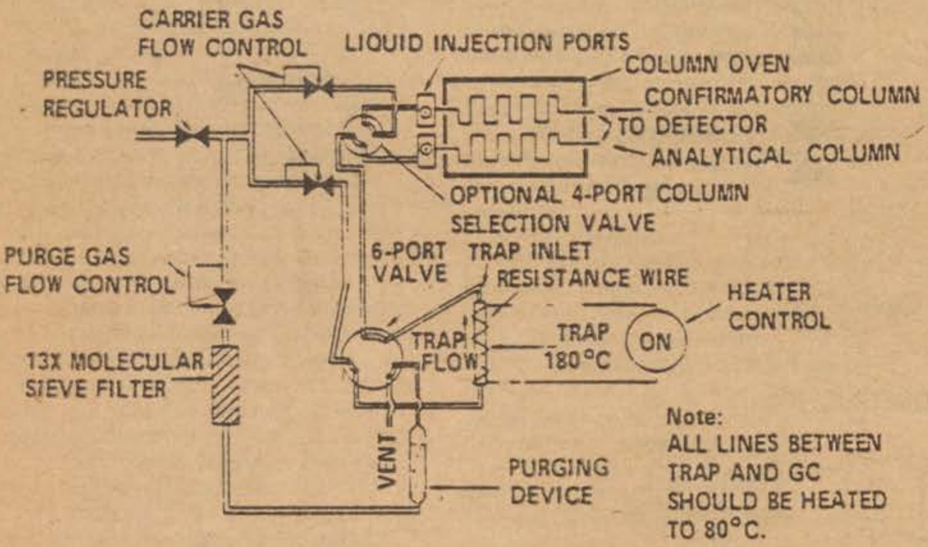

Figure 4. Schematic of purge and trap device - desorb mode

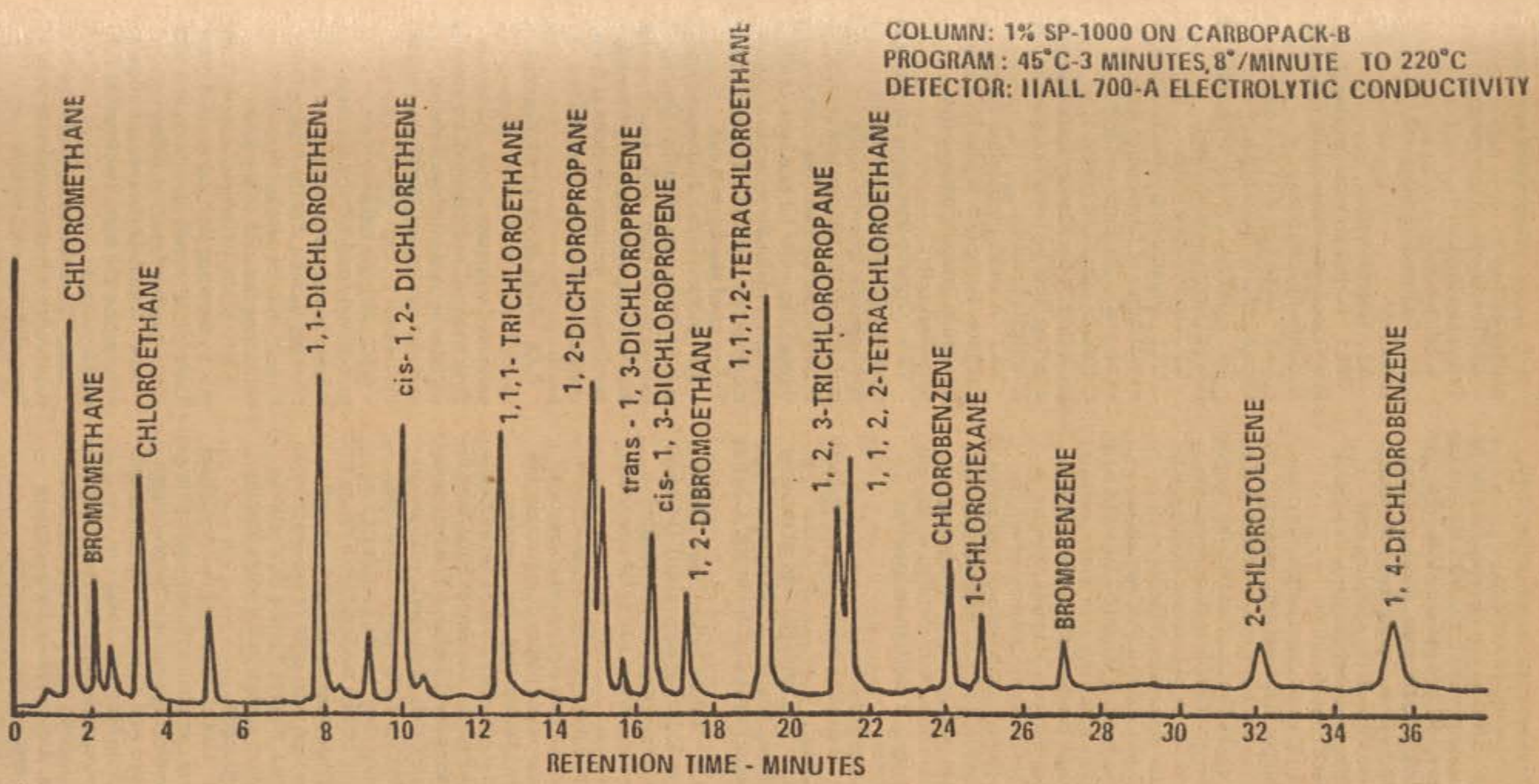

Figure 5. Gas chromatogram of purgeable halocarbons

BILLING CODE 6560-01-C

Purgeable Aromatics—Method 602

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.*
Benzene	34030
Chlorobenzene	34301
1,2-Dichlorobenzene	34536
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
Ethylbenzene	34371
Toluene	34010

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed purging chamber. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a short sorbent tube where the aromatics are trapped. After the purge is completed, the trap is heated and backflushed with gas to desorb the aromatic compounds into a gas chromatographic system. A temperature program is used in the GC system to separate the aromatics before detection with a photoionization detector.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants or flow controllers with rubber components in the purging device 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 sample blank prepared from organic free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of aromatics, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

4.1.2 Septum-Teflon-faced silicone (Pierce §12722 or equivalent). Detergent wash, rinse, with tap and distilled water, and dry at 105° C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Several complete devices are available commercially. The device must meet the following specifications: The unit must be completely compatible with the gas chromatograhpic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in Figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including Model PI-51-02 photoionization detector (h-nu Systems, Inc.), column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hyodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe value with Luer ends (3 each).

4.7 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Reagents.*

5.1 Solium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.2 Three percent OV-1 on Chromosorb-W 60/80 mesh.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water purification system (millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

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

5.5 Stock standards—Prepare stock standard solutions in methyl alcohol using assayed liquids. Because benzene an 1,4-dichlorobenzene are suspected carcinogens, primary dilutions of these compounds should be prepared in a hood.

5.5.1 Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Using a 100 µl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in mircograms per microliter from the net gain in weight.

5.5.5 Store stock standards at 4°C. All standards must be replaced with fresh standard each month.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the analytical system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20.0 µl of standard in methyl alcohol to 100, 500, or 1000 ml of organic-free water. A 25 µl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble th necessary purge and trap device. The Trap must meet the minimum specifications shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180°C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 8. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978) before reliable sample analysis may begin.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of 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 blank with surrogate compounds (e.g. *aaa*-trifluorotoluene).

8. *Sample Collection, Preservation, and Handling.*

8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to about 2 by adding 1:1 diluted HCl while stirring vigorously. If the sample contains free or combined chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 ml 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.

8.2 The samples must be iced or refrigerated from the time of collection until extraction.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it overflows. 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 the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.3 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.

9.4 Close both valves and purge the sample for 12.0 ± .05 minutes.

9.5 After the 12 minute purge time, disconnect the purge chamber from the trap. Dry the trap by maintaining a flow rate of 40 cc/min dry purge gas for 6 min. Attach the trap to the chromatograph, and adjust the device to the desorb mode. 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 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 50°C.

9.6 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 organic-free water.

9.7 After desorbing the sample for approximately four minutes recondition the trap by returning the purge and trap device 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 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.

9.8 Table 1 summarized the recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentration levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (µg/l) vs. peak height or area units.

10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, Vol. 66, No. 12, Dec. 1974, pp. 739–744.

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3. Bellar, T. A., and J. J. Lichtenberg, "The Determination of Purgeable Aromatic

Compounds in Drinking Waters and Industrial Wastes," (In preparation).

4. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11—Purgeables and Category 12—Acrolein, Acrylonitrile, and Dichlorodifluoromethane." Report for EPA Contract 68–03–2635 (In preparation).

Table 1.—*Chromatography of Aromatics Using Purge and Trap Method*

Compound	Retention time (min.) Col. 1 [1]	Detection limit µg/l [2]
Benzene	3.33	(3)
Toluene	5.75	(3)
Ethyl benzene	8.25	(3)
Chlorobenzene	9.17	(3)
1,4-Dichlorobenzene	16.8	(3)
1,3-Dichlorobenzene	18.2	(3)
1,2-Dichlorobenzene	25.9	(3)

[1] Supelcoport 100/120 mesh coated with 5% SP-2100 and 1.75% Bentone-34 packed in a 6 ft. x 0.085 in ID stainless steel column with helium carrier gas at 36 cc/min flow rate. Column temperature held at 50°C for 2 min. then programmed at 6°C/min. to 90°C for a final hold.

[2] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, using a h-nu Model PI-51-02 photoionization detector with a 10.2 ev lamp.

[3] Not determined.

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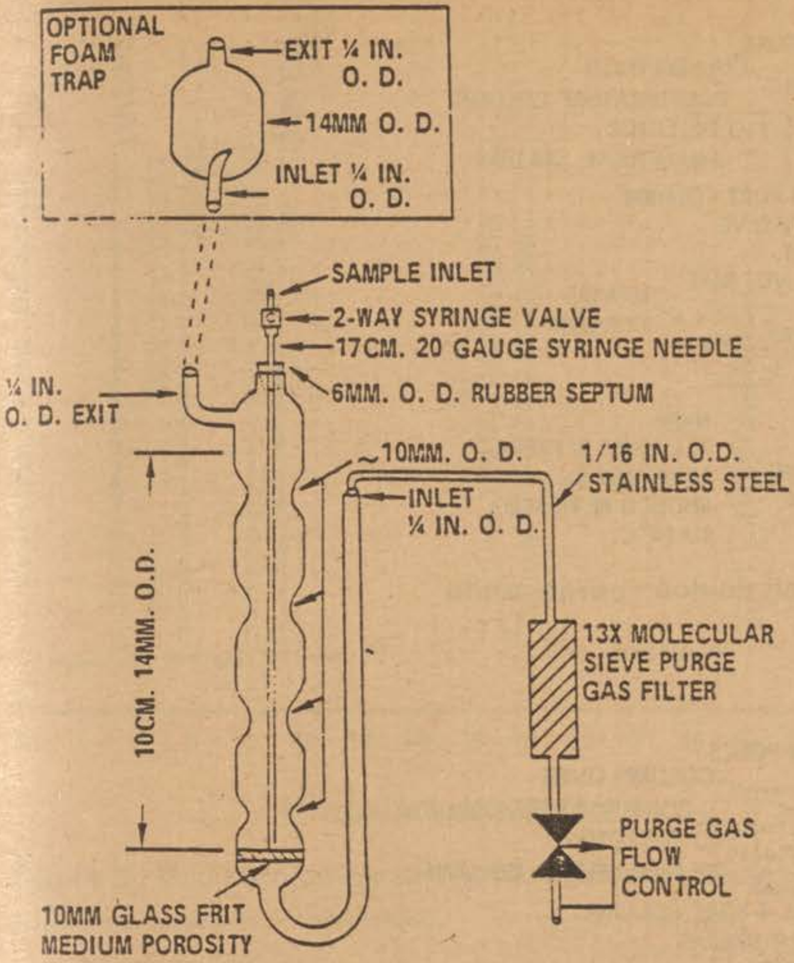

Figure 1. Purging device

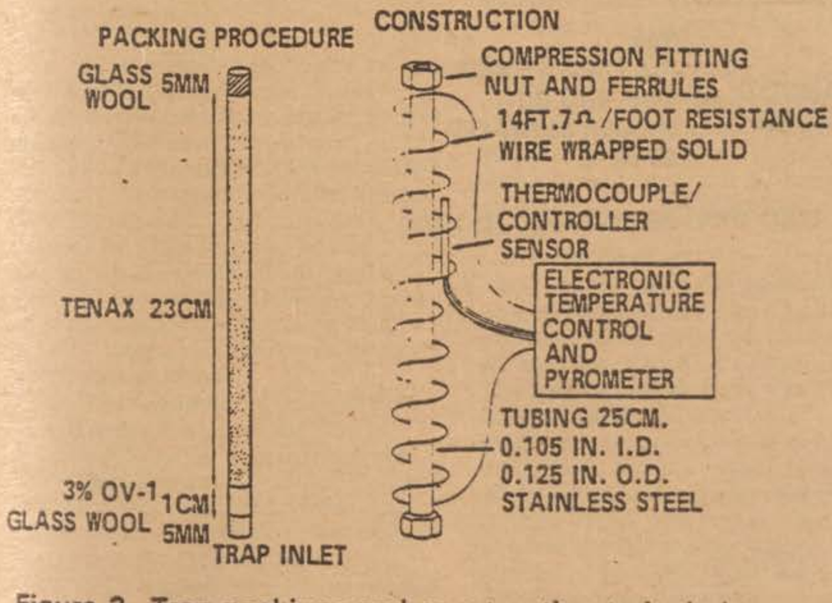

Figure 2. Trap packings and construction to include desorb capability

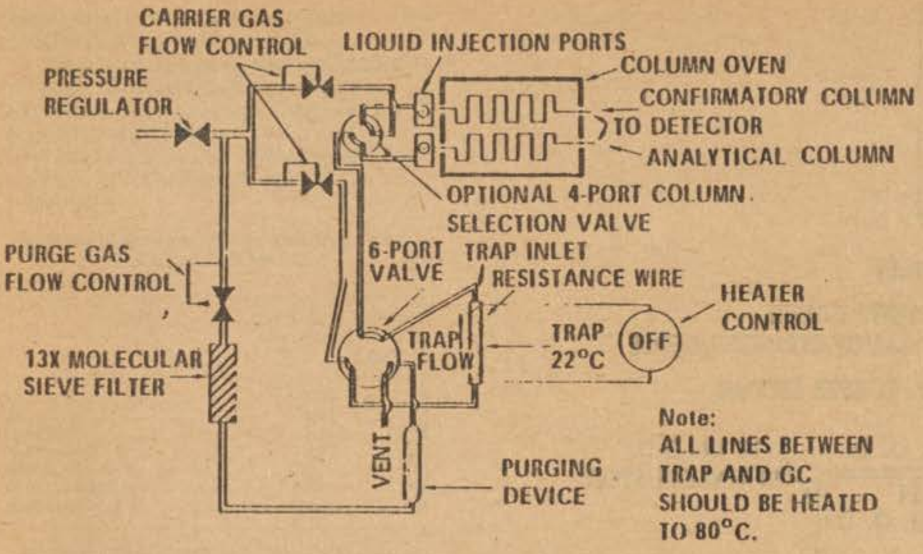

Figure 3. Schematic of purge and trap device - purge mode

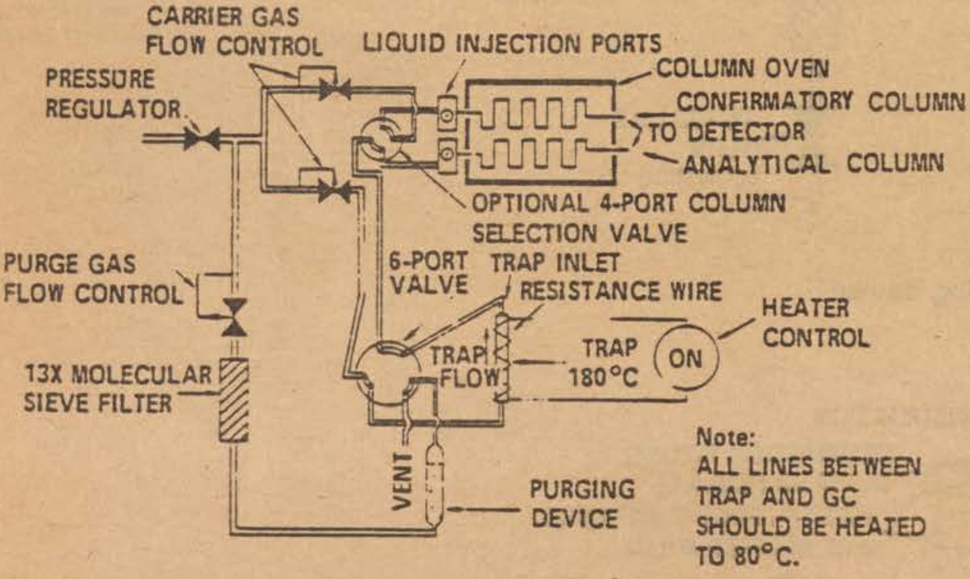

Figure 4. Schematic of purge and trap device - desorb mode

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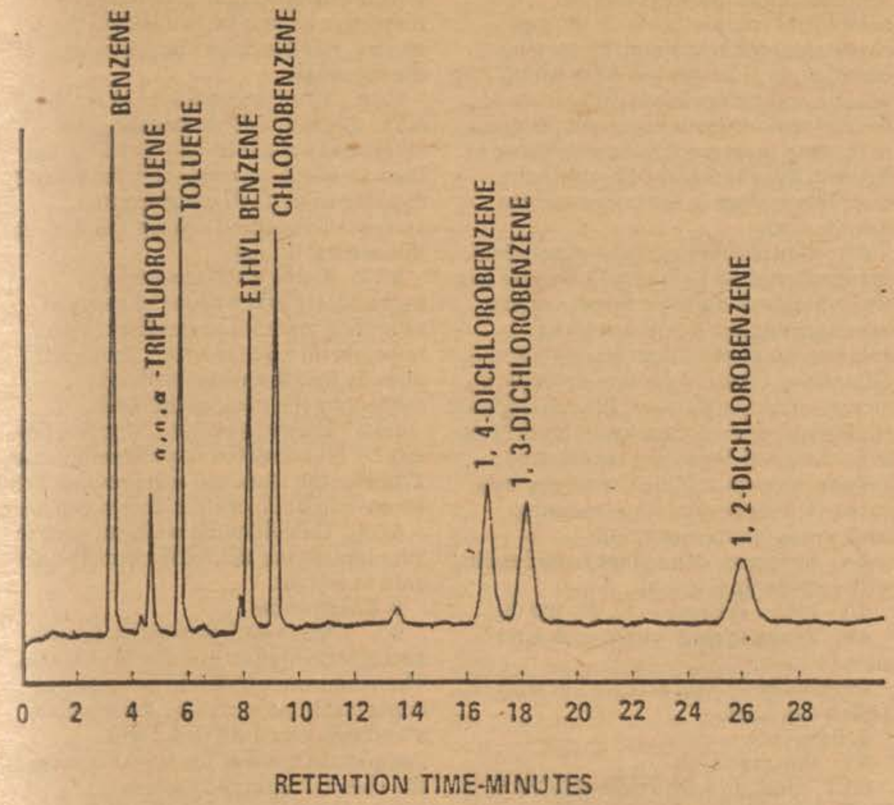

Figure 5. Gas chromatogram of purgeable aromatics

Acrolein and Acrylonitrile—Method 603

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.*
Acrolein	34210
Acrylonitrile	32415

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is passed through a short sorbent tube where the compounds are trapped. After the extraction is completed, the trap is heated and backflushed with gas to desorb the compounds into a gas chromatographic system. A temperature program is used in the GC system to separate the compounds before detection with a flame ionization detector.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free 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 soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Interferences are sometimes reduced or eliminated by first purging the water samples for 5 minutes at room temperature in 9.4. Then the purge device is rapidly heated to 85° C and purged as in 9.4. With such a modification, approximately 5 to 10% of the acrylonitrile and a trace of the acrolein in the sample will be lost. Therefore, calibration must be established for the compounds under the conditions of this modified procedure.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

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

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. The purging device should be equipped for heating in the same manner as the trap (electrically) or with a circulating water jacket. If electrical heating is used the electrical parts must be protected so that water will not drip on the conductors, causing dangerous electrical shock or shorts. All temperature parameters must be carefully controlled. Several complete devices are available commercially although most are not equipped to heat the purging chamber. The device must meet the following specifications: the unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection, equipped with matched columns for dual column analysis and a differential flame ionization detector. A nitrogen specific detector (thermionic or Hall) may be used if only acrylonitrile is to be detected. Required accessories include: column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 ul.

4.6 2-way syringe valve with Luer ends (3 each).

4.7 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Reagents.*

5.1 Preservatives

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2. Sulfuric acid—(ACS). Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Trap absorbent—Porous polymer packing, 50/80 mesh chromatographic grade Porapak N.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water.

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

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

5.5 Stock standards—Prepare stock standard solutions daily in water using assayed standards. Because of toxicity, 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 the materials.

5.5.1 Place about 9.8 ml of water (pH 6.5 to 7.5) into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all water wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the water without contacting the neck of the flask.

5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in water. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the chromatographic system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20 ul of stock standard to 100, 500, or 1000 ml of organic-free water.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards should be 85±5% for acrolein and 98±5% for acrylonitrile.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of 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 blank with surrogate compounds.

8. *Sample Collection, Preservation, and Handling.*

8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to 6.5 to 7.5 by adding 1:1 diluted H_2SO_4 or NaOH while stirring vigorously. If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 ml sample bottle and seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

8.3 All samples must be analyzed within 3 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Adjust the helium purge gas flow rate to 20±1 ml/min and the temperature of the purge device to 85°C. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it oveflows. 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.

9.3 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.

9.4 Close both valves and purge the sample for 30.0±0.1 minutes. Monitor and control the temperature of the purge device to obtain 85±1°C.

9.5 After the 30-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly hearing the trap to 170°C while backflushing the trap with helium at 45 ml/min for 5 minutes. The backflushing time and gas flow rate must be carefully reproduced from sample to sample. During blackflushing the chromatographic column is held at 100°C. Record GC retention time from the beginning of desorption.

9.6 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 organic-free water.

9.7 After desorbing the sample for 5 minutes recondition the trap by returning the purge and trap device to the purge mode and begin the GC progrm. 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°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.

9.8 Table 1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentrations levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (ug/l) vs. peak height or area units.

10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. *Accuracy and precision*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. Bellar, T.A., and J.J. Lichtenberg, Journal American Water Works Association, Vol. 66, No. 12, Dec. 1974, pp. 739–744.

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4. Going, John, et al., "Environmental Monitoring Near Industrial Sites-Acrylonitrile," EPA Report No. 560/6–79–003, 1979.

Table 1.—*Gas Chromatography by Heated Purge and Trap*

Compound [1]	Retention Time (min.)	Detection Limit ug/1 [2]
Acrolein	7.6	2
Acrylonitrile	8.9	

[1] Column conditions: Chromosorb 101 80/100 mesh packed in a 6' × ⅛" O.D. stainless steel column with helium carrier gas at 45 m1/min flow rate. Column temperature is held at 100° C for 5 minutes during trap desorption, then programmed at 10 ° C/min to 140 °C and held for 5 minutes.

[2] Detection limit is estimated, based upon the use of a flame ionization detector.

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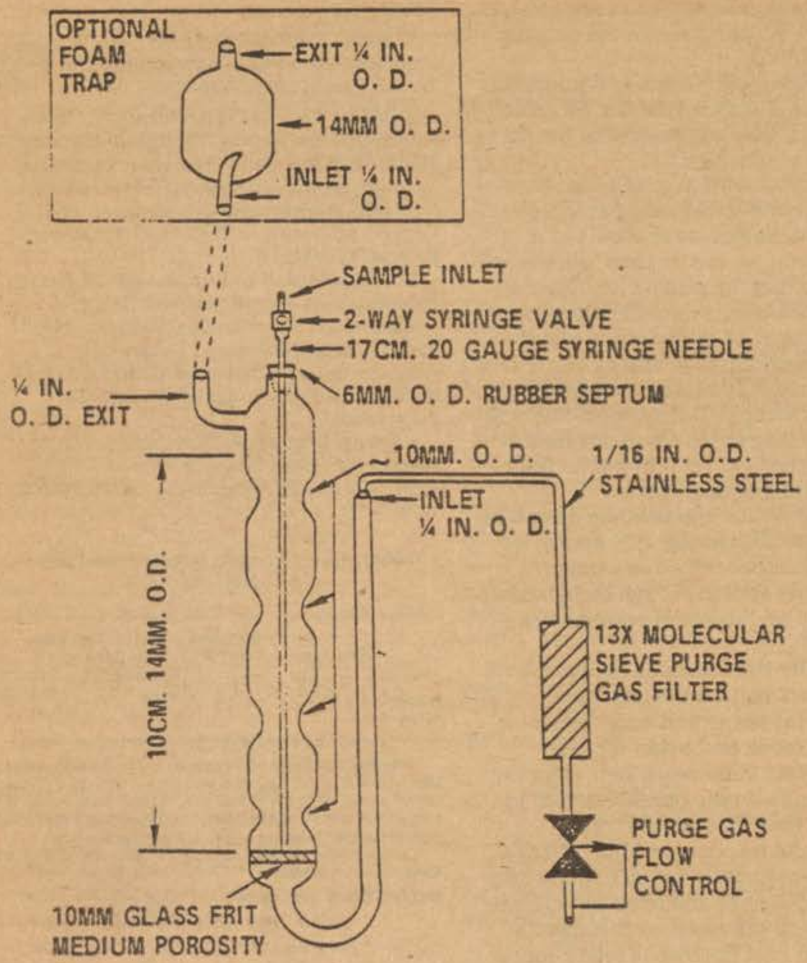

Figure 1. Purging device

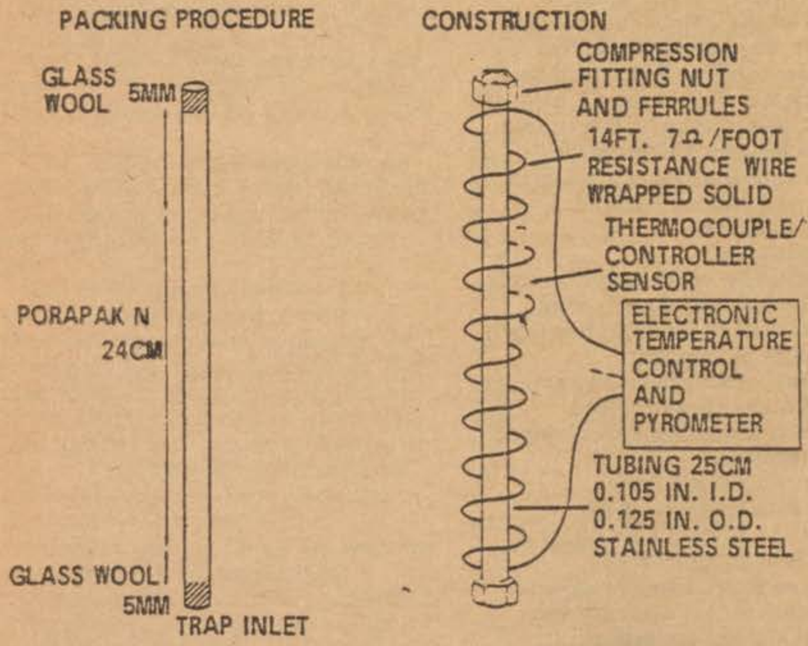

Figure 2. Trap packings and construction to include desorb capability

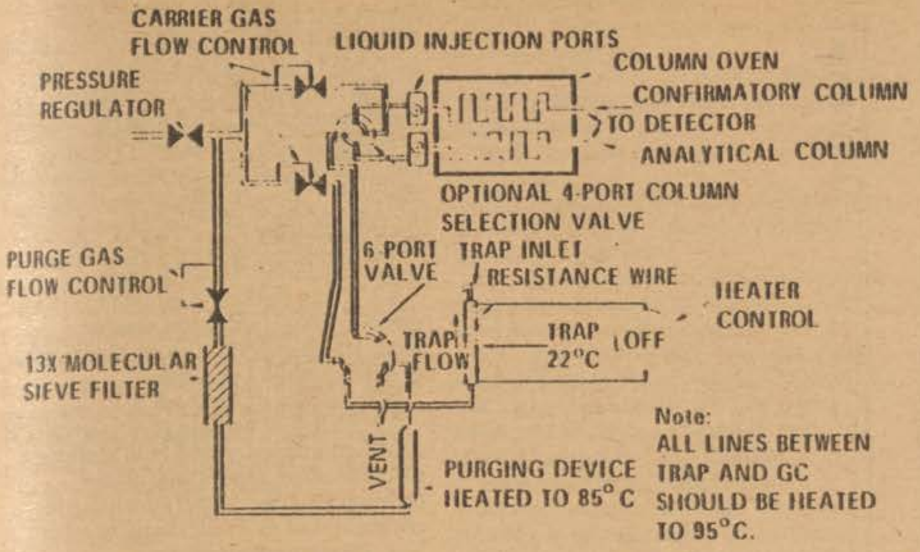

Figure 3. Schematic of purge and trap device - purge mode

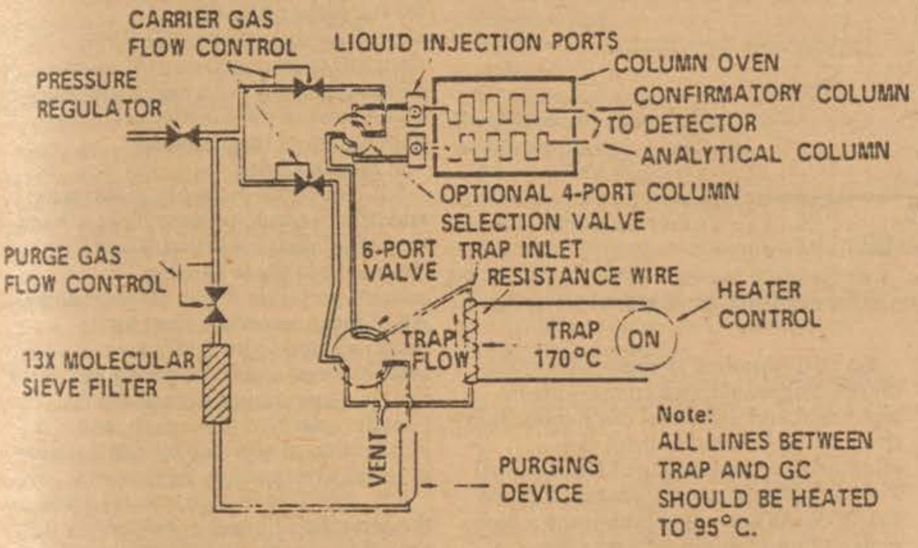

Figure 4. Schematic of purge and trap device - desorb mode

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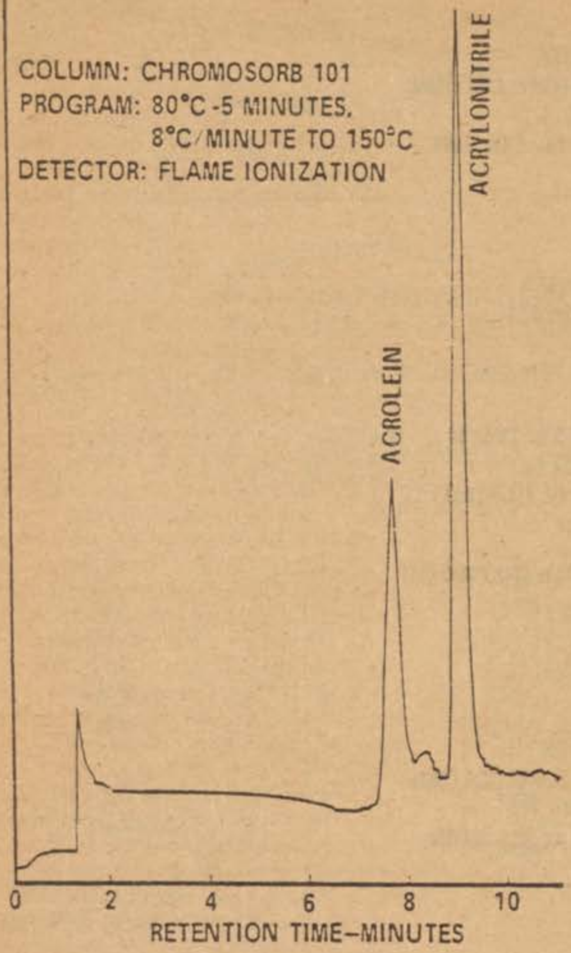

Figure 5. Gas chromatogram of acrolein and acrylonitrile

Phenols—Method 604

1. *Scope and Application.*

1.1 This method covers the determination of various phenolic compounds. The following parameters may be determined by this method:

Parameter	*Storet No.*
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39094
Phenol	34694
2,4,6-Trichlorophenol	34621

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters with a flame ionization detector in the absence of interferences. If the derivatization cleanup is required, the sensitivity of the method is 10 $\mu g/1$. This concentration represents the minimum amount proven to date to give reproducible and linear response during derivatization.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is acidified and extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Flame ionization gas chromatographic conditions are described which allow for the measurement of the compounds in the extract.

2.2 The method also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives for electron capture gas chromatography with additional cleanup procedures to aid the analyst in the elimination of interferences.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minumum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in this system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID Pyrex chromatographic column with coarse frit.

4.4. Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including flame ionization and electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—10 mm ID by 100 mm length, with Teflon stopcock.

4.8 Reaction vial—20 ml, with Teflon-lined cap.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(1+1) Mix equal volumes of conc. H_2SO_4 (ACS) with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Methylene chloride, acetone, 2-propanol, hexane, toluene—Pesticide quality or equivalent.

5.3 Sodium sulfate—(ACS) Granular, anhydrous (purified by heating at 400° C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 $\mu g/\mu l$ by dissolving 0.100 grams of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Sulfuric acid—(ACS) 1 N in distilled water.

5.6 Potassium carbonate—(ACS) powdered.

5.7 Pentafluorobenzyl bromide (a-Bromopentafluorotoluene)—97% minimum purity.

5.8 1,4,7,10,13,16—Hexaoxacyclooctadecane (18 crown 6)—98% minimum purity.

5.9 Derivatization reagent—Add 1 ml pentafluorobenzyl bromide and 1 gram 18 crown 6 to a 50 ml volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly.

5.10 Silica gel—(ACS) 100/200 mesh, grade 923; activated at 130°C and stored in a sesiccator.

6. *Calibration.*

6.1 Prepare calibration standards for the flame ionization detector that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 $\mu g/l$ in the final extract, for example, prepare standards at 10 $\mu g/l$, 50 $\mu g/l$, 100 $\mu g/l$, 500 $\mu g/l$, etc. so that injections of 1-5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using the derivatization clean up procedure, the analyst must process a series of calibration standards through the procedure to validate the precision of the derivatization and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg of sodium thiosulfate per part per million free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid solution or 10N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the sample pH to 12 with sodium hydroxide.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for one minute with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechnical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Discard the methylene chloride layer, and wash the sample with an additional two 60 ml portions of methylene chloride in similar fashion.

9.3 Adjust the aqueous layer to a pH of 1–2 with sulfuric acid.

9.4 Add 60 ml of methylene chloride to the sample and shake for two minutes. Allow the solvent to separate from the sample and collect the methylene chloride in a 250 ml Erlenmeyer flask.

9.5 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract the through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.7 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the appartus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.8 Increase the temperature of the hot water bath to 95–100°C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of 2-propanol. A 5-ml syringe is recommended for this operation. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 ml 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 5–10 minutes. 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 2.5 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. 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 for at least 10 minutes while cooling. 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 in refrigerator, if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with flame ionization gas chromatographic analysis. If the sample requires cleanup, proceed to section 11.

9.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. After correction for sulfuric acid preservative, record the sample volume to the nearest 5 ml.

10. *Gas Chromatography-Flame Ionization Detector.*

10.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by one of these columns is shown in Figure 1. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.

10.2 Inject 2–5 μl of the sample extract 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 units.

10.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

10.4 If the peak area measurement is prevented by the presence of interferences, the phenols must be derivatized and analyzed by electron capture gas chromatography.

11. *Derivatization and Electron Capture Gas Chromatography.*

11.1 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 derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/ml.

11.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

11.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.

11.4 Remove the solution from the hot water bath and allow it to cool.

11.5 Add 10 ml hexane to the reaction vial and shake vigorously for one minute. Add 3.0 ml of distilled, deionized water to the reaction vial and shake for two minutes.

11.6 Decant organic layer into a concentrator tube and cap with a glass stopper.

11.7 Pack a 10 mm ID chromatographic column with 4.0 grams of activated silica gel. After settling the silica gel by tapping the column, add about two grams of anhydrous sodium sulfate to the top.

11.8 Pre-elute the column with 6 ml hexane. Discard the eluate and just prior to exposure of the sulfate layer to air, pipet onto the column 2.0 ml of the hexane solution (11.6) that contains the derivatized sample or standard. Elute the column with 10.0 ml of hexane (Fraction 1) and discard this fraction. Elute the column, in order, with: 10.0 ml 15% toluene in hexane (Fraction 2); 10.0 ml 40% toluene in hexane (Fraction 3); 10.0 ml 75% toluene in hexane (Fraction 4); and 10.0 ml 15% 2-propanol in toluene (Fraction 5). Elution patterns for the phenolic derivatives are shown in Table II. Fractions may be combined as desired, depending upon the specific phenols of interest or level of interferences.

11.9 Analyze the fractions by electron capture gas chromatography.

Table II summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times that should be achieved by this method. Examples of the separation achieved by this column is shown in Figure 2. 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 the procedure.

11.10 Inject 2–5 μl of the column fractions 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 units. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

12. *Calculations*

12.1 Determine the concentration of individual compounds measured by the flame ionization procedure (without derivatization) according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (μl)

12.2 Determine the concentration of individual compounds measured by the derivatization and electron capture procedure according to the following procedure:

12.2.1 From the concentration of the calibration standards that were derivatized with the samples, calculate the amounts, in nanograms, of underivatized phenols that were added as 2-propanol solution (11.1). From the size of the injection into the electron capture gas chromatograph, determine the nanograms of material (calculated as the underivatized phenol) injected onto the column. Compare the detector responses obtained to develop a calibration factor for the chromatographic system, in nanograms of material per area unit.

12.2.2 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/1 = \frac{(A)(B)(V_t)(10)(D)}{(V_i)(V_s)(C)(E)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit, calculated as underivatized phenol.

B = Peak size in injection of sample extract, in area units.

V_i = Volume of eluate injected (μl)

V_t = Total volume of column eluate (μl)

V_s = Volume of water extracted (ml)

C = Volume of hexane sample solution added to cleanup column, in ml.

D = Total volume of 2-propanol extract after concentration.

E = Volume of 2-propanol extract used for derivatization.

12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3—Chlorinated Hydrocarbons and Category 8—Phenols." Report for EPA Contract 68-03-2625 (In preparation).

Table I.—*Flame Ionization Gas Chromatography of Phenols*

Compound [1]	Retention time	Detection limit (μg/L) [2]
2-Chlorophenol	1.70	2.0
2-Nitrophenol	2.00	2.5
Phenol	3.01	1.4
2,4-Dimethylphenol	4.03	1.7
2,4-Diclorophenol	4.30	2.1
2,4,6-Trichlorophenol	6.05	5.0
4-Chloro-3-methylphenol	7.50	8.3
2,4-Dinitrophenol	10.00	7.0
2-Methyl-4,6-dinitrophenol	10.24	10.0
Pentachlorophenol	12.42	10.0
4-Nitrophenol	24.25	10.0

[1] Column conditions: Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 6 ft long×2 mm ID glass column with nitrogen carrier gas at 30 ml/min flow rate. Column temperature is 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature.

[2] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final extract volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

Table II.—*Electron Capture Gas Chromatography of PFB Derivatives*

Parent compound [1]	Rentention time (minutes)	Recovery percent by fraction [2]				
		1	2	3	4	5
2-chlorophenol	3.3			90	>1	
2-nitrophenol	9.1				9	90
Phenol	1.8			90	10	
2,4-Dimethyphenol	2.9			95	7	
2,4-Dichlorophenol	5.8			95	>1	
2,4,6-Trichlorophenol	7.0		50	50		
4-Chloro-2-methyphenol	4.8			84	14	
Pentach lorophenol	28.8		75	20		
4-Nitrophenol	14.0				>1	90
(2,4-Dinitrophenol)	[3]46.9					
(2-Methyl-4,6-dinitrophenol	[3]36.6					

[1] 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 is 200°C.

[2] From: "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Categories 3-Chlorinated Hydrocarbons and Category 8-Phenols."

[3] Retention times included for qualitative information only. The lack of accuracy and precision of the derivatization reaction precludes the use of this approach for quantitative purposes.

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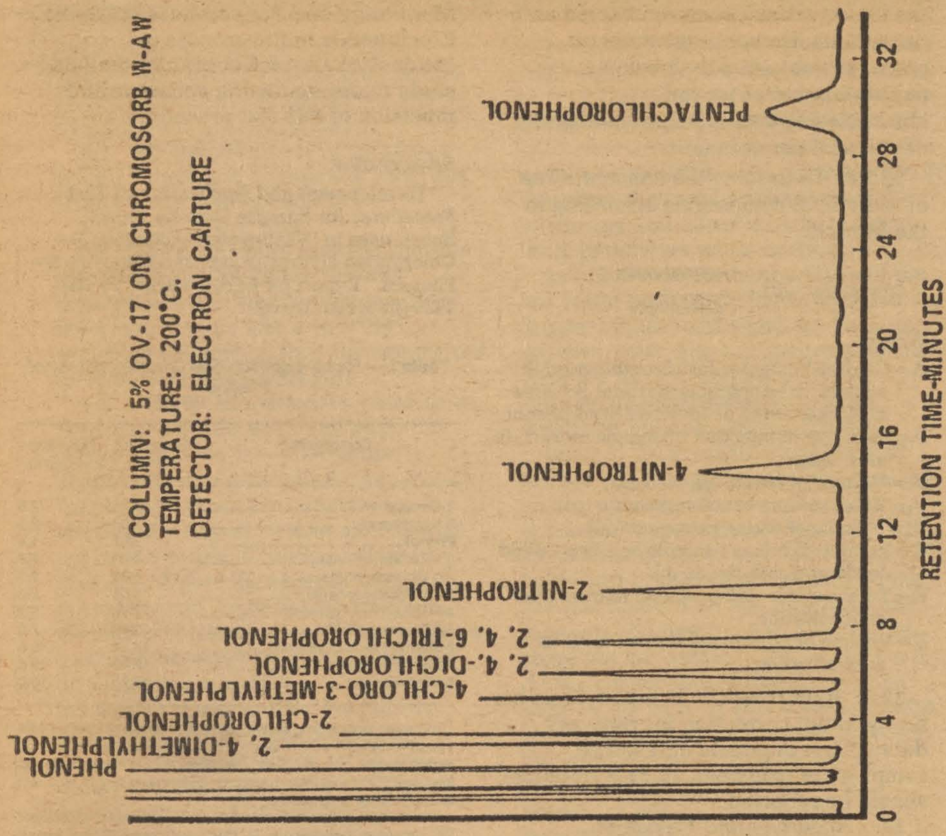

Figure 2. Gas chromatogram of PFB derivatives of phenols

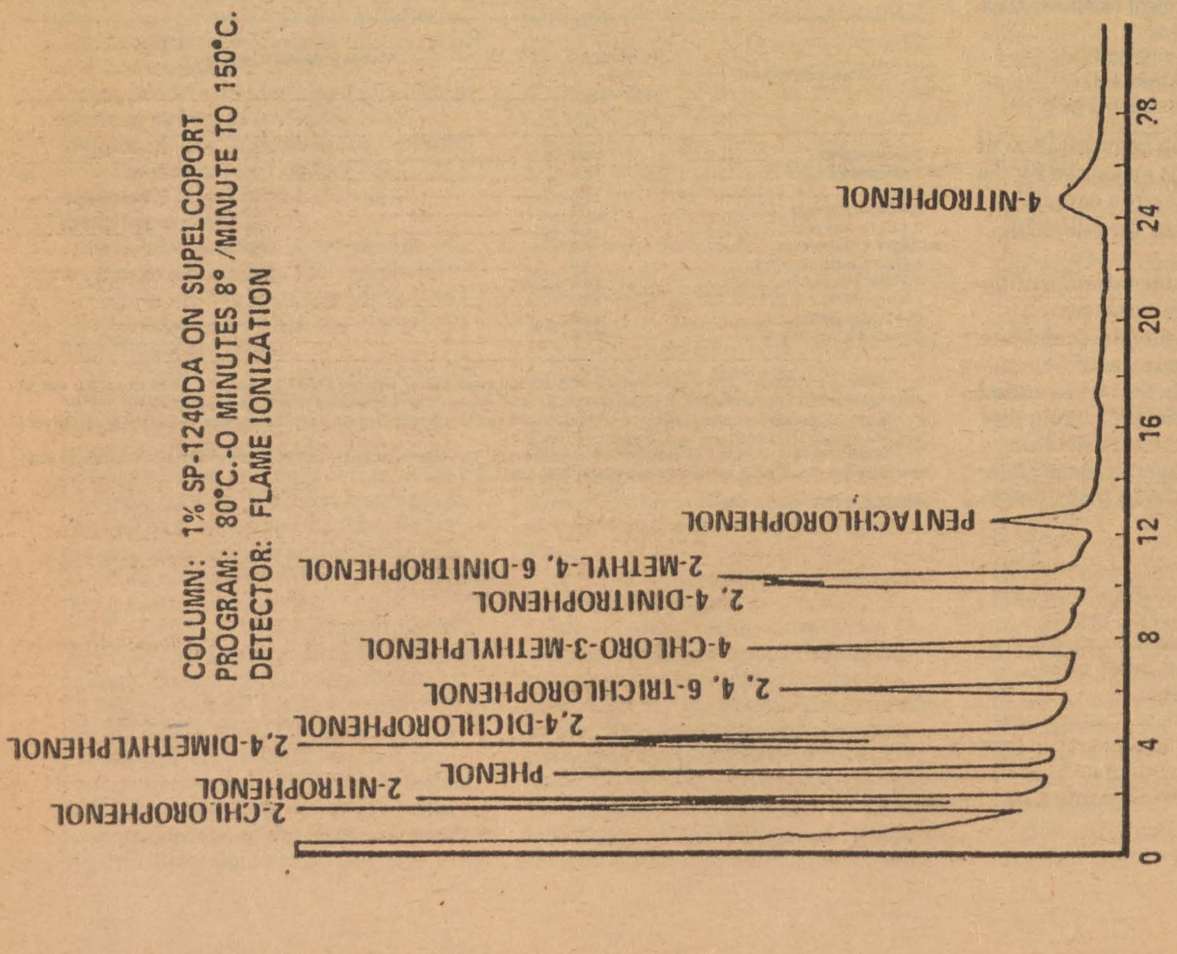

Figure 1. Gas chromatogram of phenols

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Benzidines—Method 605

1. *Scope and Application.*

1.1 This method covers the determination of benzidine and selected derivatives. The following parameters may be determined by this method:

Parameter:	*Storet No.*
Benzidine	39120
3,3'-Dichlorobenzidine	34631

1.2 This method is applicable to the measurement of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identifications implied with the use of these techniques.

1.3 This sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 Benzidine and 3,3-dichlorobenzidine (DCB) are extracted from the sample at pH 7–8 using chloroform. The extract is then back extracted into acid, re-extracted into chlorofom at neutral pH, and concentrated. The benzidines are determined in the final extract using high performance liquid chromatography (HPLC) with electrochemical detection.

2.2 If interferences are encountered with the measurement of benzidine, the method provides additional detector settings to increase the selectivity of the analytical system.

3. *Interferences.*

3.1 Although the detection system is highly selective, solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Some dye plant effluents contain large amounts of components with retention times in the vicinity of benzidine. In these cases, it has been found useful to reduce the electrode potential in order to eliminate the interferences but still detect the benzidine.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-pint or 1-quart volume. Quart bottles should be only half filled in the field. French or Boston Round design is recommended. The container should be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if the sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing or fittings may be used in the system.

4.2 Separatory funnel—1000 ml and 250 ml, with Teflon stopcock.

4.3 Water bath—Heated, with concentric ring cover, capable of temperature control within 2°C. The bath should be used in a hood.

4.4 Rotating evaporator.

4.5 Flasks—round bottom, 100 ml, with 24/40 joints.

4.6 Centrifuge tubes—conical, screw capped, graduated, with Teflon lined caps.

4.7 Pipettes—Pasteur, with bulbs.

4.8 High performance liquid chromatograph—Analytical system complete with column supplies, recorder, syringes, and the following components:

4.8.1 Solvent delivery system—with pulse damper (Altex 110A, or equivalent).

4.8.2 Injection valve Waters Model USK (or equivalent).

4.8.3 Electrochemical detector Bioanalytical Systems LC–2A with glassy carbon electrode, (or equivalent).

4.8.4 Electrode polishing kit Princeton Applied Research Model 9320 (or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes in conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) granular.

5.2 Sulfuric acid (1M)—(ACS) 58 ml/liter in distilled water.

5.3 Sodium hydroxide (20%)—(ACS) 20 grams/100 ml in distilled water.

5.4 Sodium hydroxide (IM)—(ACS) 40 grams/liter in distilled water.

5.5 Sodium tribasic phosphate (0.4M)—(ACS) 160 grams Na_3PO_4 $(12H_2O)$ in 1 liter of distilled water.

5.6 Acetate buffer 0.1*M*, pH 4.7; 5.8 mls glacial acetic acid (ACS) and 13.6 grams of sodium acetate trihydrate (ACS) per liter in distilled water.

5.7 Acetonitrile—Pesticide quality or equivalent.

5.8 Methyl alcohol—Pesticide quality or equivalent.

5.9 Chloroform (preserved with 1% ETOH)—Burdick and Jackson (or equivalent).

5.10 Water—Purified (e.g. from Millipore RO–4 System or equivalent).

5.11 HPLC mobile phase—Place 1 liter of filtered (through Millipore type FH filter, or equivalent) acetonitrile and 1 liter of filtered (through Millipore type GS filter, or equivalent) acetate buffer in a narrow mouth, glass, one gallon jug and mix thoroughly. Prepare fresh weekly.

5.12 Stock standards—Prepare stock standard solutions at a concentration of 0.100 ug/μl by dissolving 0.0100 gram of assayed reference material in pesticide quality methyl alcohol and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared from the stock standards at the following concentrations that will bracket the working range of the chromatographic system:

Solution Conc. (ng/μl)	Sensitivity (nA Full Scale)
0.05	10
0.10	10
0.50	50
1.0	100
5.0	500

6.2 Assemble the necessary liquid chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I.

6.3 A constant injection volume of 25 microliters should be employed for all subsequent measurements.

6.4 In order to determine the precision of the HPLC system, a series of 6 replicate injections of a 1 ng/μl solution of benzidine and 3,3'-dichlorobenzidine (DCB) should be made on the 50nA full scale setting. A precision of ±4% should be achieved for the peak heights of both benzidine and DCB. This measurement should be made every few weeks or whenever instrument related problems are apparent. A sample chromatogram is shown in Figure 1.

6.5 Retention times should remain relatively constant (within ±5% day to day) with benzidine being 6.1 minutes and DCB being 12.1 minutes under the specified conditions. These values should be checked daily when the calibration injections are made.

6.6 If serious loss of response occurs, it may be necessary to polish the surface of the carbon electrode (according to the instructions supplied with the polishing kit). In this case, it will be necessary to recalibrate the system.

6.7 When leaving the instrument idle, it is advisable to maintain a flow of 0.1 ml/min of mobile phase through the HPLC column in order to prolong column life.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection to extraction. Benzidine and dichlorobenzidine are easily oxidized by materials such as free chlorine. For chlorinated wastes, *immediately* add 35 mg sodium thiosulfate per part per million of free chlorine per liter.

8.3 If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4 ±0.2 units to prevent rearrangement to benzidine. Otherwise, if the samples will not be extracted within 48 hours of collection, the sample pH should be adjusted to 2–3 with sodium hydroxide or sulfuric acid.

8.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Quantitatively pour the entire sample into a one-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 6.5–7.5 with sodium hydroxide or sulfuric acid.

9.2 Add 100 ml chloroform to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes. Allow the organic layer to separate from the sample a minimum of ten minutes, then collect the chloroform extract in a 250-ml separatory funnel.

9.3 Add 50 ml chloroform to the sample bottle and complete the extraction procedure a second time, combining the extracts in the separatory funnel. Perform a third extraction in the same manner with an additional 50 ml volume.

9.4 Discard any aqueous layer from the 250 ml funnel containing the combined organic layers. Add 25 ml of 1 M sulfuric acid and extract the sample by shaking the funnel for two minutes. 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.

9.5 Place a stirbar in the 250 ml beaker and stir the acid extract while carefully adding 5 ml of a .4M sodium tribasic phosphate. With the aid of a pH meter neutralize the extract to pH 6–7 by dropwise addition of 20 percent NaOH while stirring the solution vigorously. Approximately 25–30 ml of 20 percent NaOH will be required and it should be added over at least a 2-minute period. Do not allow the sample pH ever to exceed pH 8.

9.6 Pour the neutralized extract into a 250 ml separatory funnel. Add 30 ml of chloroform and shake the funnel for 2 minutes. Allow phases to separate, and transfer the organic layer in a second 250 ml separatory funnel.

9.7 Extract the aqueous layer with two additional 20 ml aliquots of chloroform as before. Combine the extracts in the 250 ml separatory funnel.

9.8 Add 20 ml of distilled water to the combined organic layers, shake for 30 seconds, and discard aqueous layer.

9.9 Transfer the organic extract into a 100 ml round bottom flask. Add 20 ml of methyl alcohol and concentrate to 5 ml on a rotating evaporator at 35°C.

9.10 Using a 9-inch Pasteur pipette, transfer the extract to a 15 ml conical scew-capped centrifuge tube. Rinse the flask, including the entire side wall, with two ml portions of methyl alcohol and combine with the original extract.

9.11 Carefully concentrate the extract to 0.5 ml using a gentle stream of nitrogen and a 30°C water bath, dilute to 2 ml with methyl alcohol, reconcentrate to 1 ml, and dilute to 5 ml with acetate buffer. Mix extract thoroughly. Stopper the ampul and store refrigerated if further processing with not be performed immediately.

9.12 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.

10. Liquid Chromatography (HPLC).

10.1 Table I summarizes the recommended liquid chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 1. Calibrate the system daily with a minimum of three injections of calibration standards.

10.2 Inject 25 ul of the sample extract. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

10.3 If the peak area measurement for benzidine is prevented by the presence of interferences, reduce the electrode potential to 0.7 V and reanalyze.

11. Calculations.

11.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per unit peak area.

B = Peak size in injection of sample extract, in peak area units

V_i = Volume of extract injected(μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

11.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

12. Accuracy and Precision.

12.1 The U.S. EPA Environmental Monitioring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters Category 7—Benzidines," Report for EPA Contract 68–03–2624 (In preparation).

Table I.—*Liquid Chromatography of Benzidines*

Compound [1]	Retention time (min.)	Detection limit (μg/l) [2]
Benzidine	6.1	0.05
3,3'-dichlorobenzidine	12.1	0.1

[1] Column conditions: Lichrosorb RP-2, 5 micron particle diameter, packed in a 25 cm × 4.6 mm ID stainless steel column with 0.8 ml/min flow rate of mobile phase (50 percent acetonitrile: 50 percent 0.1 M pH 4.7 acetate buffer).

[2] Detection limit is calculated from the minimum detectable response of the electrochemical detector at 0.8 volts being equal to five times the background noise, assuming a 5 ml final extract volume of the 500 ml sample, and assuming an injection volume of 25 microliters.

Phthalate Esters—Method 606

1. *Scope and Application.*

1.1 This method covers the determination of certain phthalate esters. The following parameters may be determined by this method:

Parameter:	*Storet No.*
Benzyl butyl phthalate	34292
Bis(2-ethylhexyl) phthalate	39100
Di-n-butyl phthalate	34110
Di-n-octyl phthalate	34596
Diethyl phthalate	34336
Dimethyl phthalate	34341

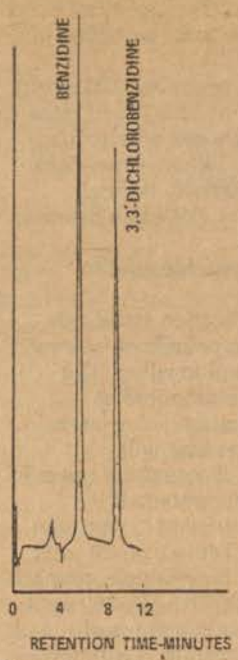

Figure 1. Liquid chromatogram of benzidines

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the sample will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis. Of particular importance is the avoidance of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture or flame ionization detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—300 mm long × 10 mm ID with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Diethyl Ether—Nanograde, redistilled in glass if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.6 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in dark in glass container with ground glass stoppers or foil-lined screw caps.

5.7 Alumina—Activity Super I, Neutral, W200 series, (ICN Life Sciences Group, No. 404583).

5.8 Hexane—Pesticide quality.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitudes that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/1 in the final extract, for example, prepare standards at 10 μg/1, 50 μg/1, 100 μg/1, 500 μg/1, etc. so that injections of 1-5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the ph of the sample pH with wide-range paper and adjust to within the range of 5-9 with sodium hydroide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size 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, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with

20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertial position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 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. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. Elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. 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 sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 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.

10. *Cleanup and Separaton.*

10.1 If the entire extract is to be cleaned up by one of the following two procedures, it must be concentrated to about 2 ml. To the concentrator tube in 9.6, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml hexane through the top. Place the 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 5–10 minutes. 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 for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of hexane. Proceed with one of the following cleanup procedures.

10.2 Florisil Column Cleanup for Phthalate Esters

10.2.1 Place 100 g of Florisil into a 500 ml beaker and heat for approximately 16 hours 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 distilled water which is free of phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.2.2 Place 10g of this Florisil preparation into a 10 mm ID chromatography column and tap the column to settle the Florisil. Add 1 cm of anhydrous sodium sulfate to the top of the Florisil.

10.2.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane complete the transfer.

10.2.4 Just prior to exposure of the sodium sulfate layer to the air add 40 ml hexane and continue the elution of the column. Discard this hexane eluate.

10.2.5 Next elute the phthalate esters with 100 ml of 20 percent ethyl ether/80 percent hexane (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K–D technique. No solvent exchange is necessary. After concentration and cooling, adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and analyze by gas chromatography.

10.3 Alumina Column Cleanup for Phthalate Esters

10.3.1 Place 100 g of alumina into a 500 ml beaker and heat for approximately 16 hours 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 distilled water which is free from phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.3.2 Place 10 g of this alumina preparation into a 10 mm ID chromatography column and tap the column to settle the alumina. Add 1 cm of anhydrous sodium sulfate to the top of the alumina.

10.3.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane to complete the transfer.

10.3.4 Just prior to exposure of the sodium sulfate layer to the air add 35 ml hexane and continue to elution of the column. Discard this hexane eluate.

10.3.5 Next elute the column with 140 ml of 20 percent ethyl ether/80 percent hexane (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K–D technique. No solvent exchange is necessary. After concentration and cooling adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract 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 units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(B_{t})}{(V_{i})(V_{s})}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volumeof water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting a interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1-Phthalates." Report for EPA Contract 68-03-2606 (In preparation).

Table I—*Gas Chromatography of Phthalate Esters*

Compound	Retention time (min.)		Detection (µg/l)	
	Col. 1	Col. 2	EC [3]	FID
Dimethyl phthalate	2.03	0.95	0.11	19
Diethyl phthalate	2.82	1.27	0.13	31
Di-n-butyl phthalate	8.65	3.50	0.02	14
Benzyl butyl phthalate	*6.94	**5.11	0.02	15
Bis(2-ethylhexyl) phthalate	*8.92	**10.5	0.04	20
Di-n-octyl phthalate	*16.2	1**8.0	0.11	31

* Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long × 4 mm ID glass column with carrier gas at 60 ml/min flow rate. Column temperature is 180°C except where * indicates 220°C. Under these conditions R.T. of Aldrin is 5.49 min. at 180°C and 1.84 min at 220°C.

** Supelcoport 100/120 mesh with 3% OV-1 in a 180 cm long × 4 mm ID glass column with carrier gas at 60 ml/min flow rate. Column temperature is 200°C except where ** indicates 220°C. Under these conditions R.T. of Aldrin is 3.18 min. at 200°C and 1.46 min. at 220°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

BILLING CODE 6560-01-M

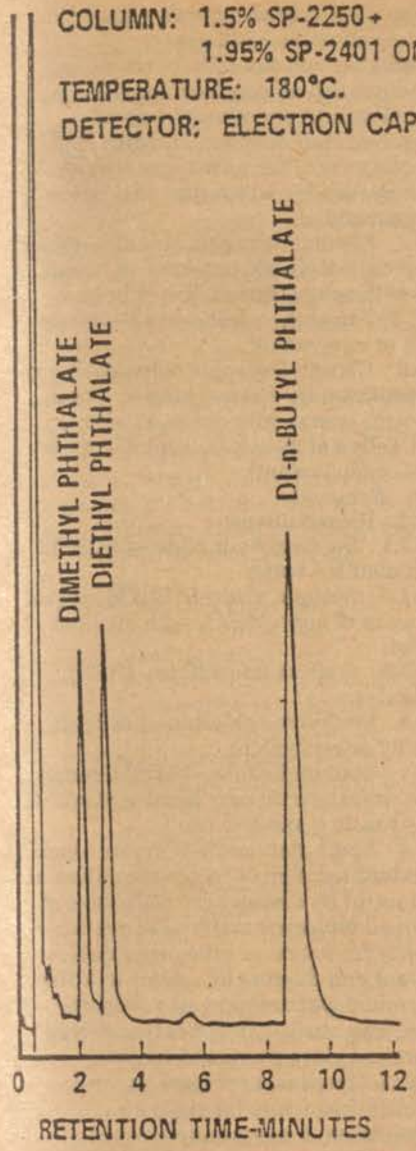

Figure 1. Gas chromatogram of phthalates

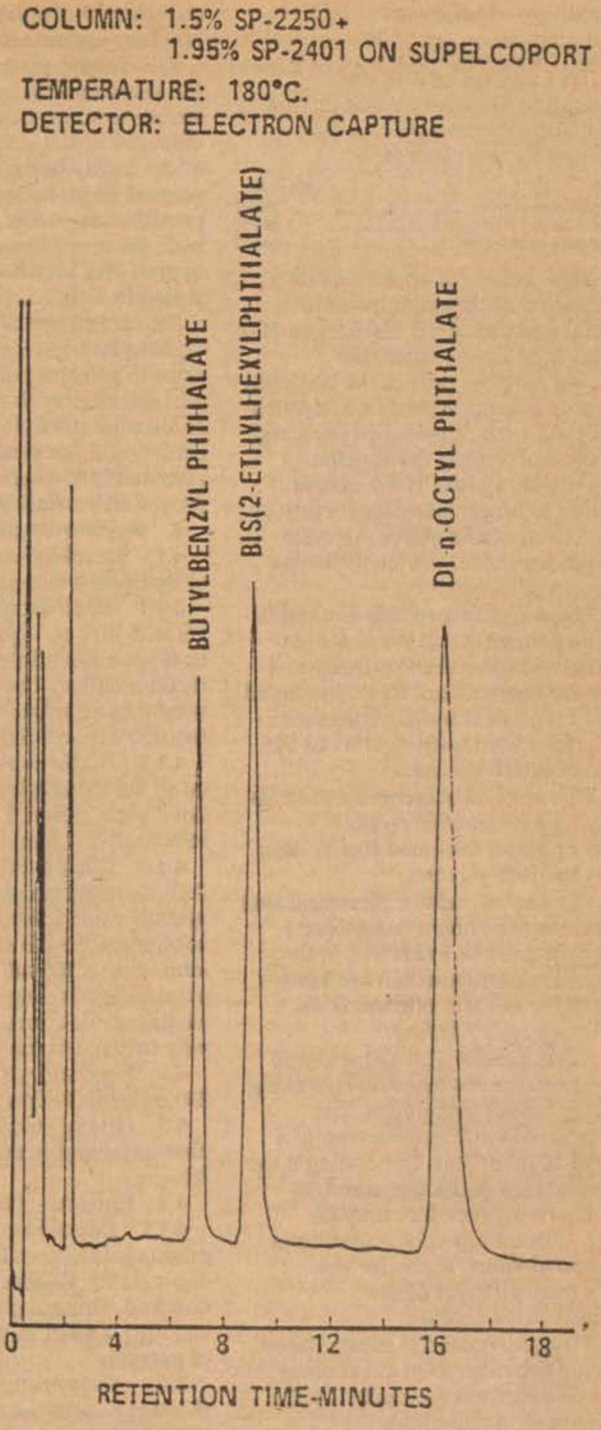

Figure 2. Gas chromatogram of phthalates

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Nitrosamines—Method 607

1. *Scope and Application.*

1.1 This method covers the determination of certain nitrosamines. The following parameters may be determined by this method:

Parameter:	*Storet No.*
N-nitrosodimethylamine	34438
N-nitrosodiphenylamine	34433
N-nitrosodi-n-propylamine	34428

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

1.5 The analyst must understand that nitrosamines are known carcinogens. Utmost care must be exercised in the handling of materials which are known or believed to contain nitrosamines.

2. *Summary of Method.*

2.1 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Depending upon the nitrosamines being measured, a column cleanup procedure may be required. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 It is necessary to remove diphenylamine from the sample extract prior to gas chromatography because it will interfere with the determination of N-nitrosodiphenylamine. Removal is achieved if the sample is processed completely through one of the clean-up procedures detailed in the method.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottle. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnels—2000 ml and 250 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including nitrogen-phosphorus or reductive Hall detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—Pyrex (approximately 300 mm long × 10 mm ID) with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0213 or equivalent).

4.8 Chromatographic column—Pyrex (approximately 400 mm long × 22 mm ID) with coarse fritted disc at bottom and Teflon stopcock (Kontes K-420540-0234 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Soidium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400° C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 $\mu g/\mu l$ by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumertic flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Methyl alcohol, pentane, acetone—Pesticide quality or equivalent.

5.6 Diethyl Ether—Nanograde, redistilled in glass if necessary.

5.6.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.6.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.7 Florisil—PR grade (60/100 mesh); purchase activiated at 1250° F and store in dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hours at 130° C in a foil covered glass container.

5.8 Alumina—Activity Super I, Basic, W200 series (ICN Life Sciences Group, No. 404571).

5.9 Hydrochloric acid, 10%-(ACS) Add one volume of conc. HCl to nine volumes distilled water.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely backet the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establishe the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectorscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 Add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to pH 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base added.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 7 to 10 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. It the emulsion interface between layers is more than one-third the size 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, or centrifugation. Collect the methylene chloride extract in a 250-ml separatory funnel.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the 250-ml separatory funnel.

9.4 Perform a third extraction in the same manner. Add 10 ml of 10% HCl solution to the combined extracts and shake for 2 minutes. Allow the layers to separate. Drain the methylene chloride layer through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in the 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. Because of the volatility of N-nitrosodimethylamine, K-D concentration must be carefully carried out. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. 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. Unless the entire extract will be subjected to a cleanup operation (Section 10), adjust the extract volume to 10.0 ml with methylene chloride, add stopper, and refrigerate.

9.6 If the sample is being analyzed for N-nitrosodiphenylamine, the analyst must immediately proceed with one of the cleanup methods in Section 10 to remove potential diphenylamine interference. Depending upon the sensitivity requirement for the analysis, the analyst may use the entire extract for this cleanup as described, or adjust the extract volume to 10.0 ml with methylene chloride and pipet a 2 ml aliquot onto the column in 10.2.2 or 10.3.3.

9.7 If N-nitrosodiphenylamine is of no interest, the analyst must choose between proceeding directly to Section II, or submitting the extract to a cleanup procedure before gas chromatography. A solvent exchange from methylene chloride to methyl alcohol is required for direct gas chromatography. Once the entire extract is in methyl alcohol it cannot be treated to either of the cleanup procedures in Section 10. Therefore, in the absence of previous experience with the sample matrix, the analyst should remove a 2.0 ml aliquot of the extract for gas chromatography and retain the remainder for cleanup if required later.

9.8 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.

10. *Cleanup and Separation.*

10.1 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 9.5, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml methylene chloride to the top. Place the K–D apparatus on a steaming hot (60–65° 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 5–10 minutes. 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 and allow it to drain for at least 10 minutes while cooling. 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.

10.2 Florisil Column Cleanup for Nitrosamines

10.2.1 Place 22g of activated Florisil in a 22 mm ID chromatographic column. After settling the Florisil by tapping the column,add about a 5 mm layer of anhydrous granular sodium sulfate to the top.

10.2.2 Preelute the column, after cooling, with 40 ml of 15% ethyl ether/85% pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to air, quantitatively transfer 2.0 ml of sample extract into the column by decantation using an additional 2 ml of pentane to complete the transfer.

10.2.3 Perform the first elution with 90 ml of 15% ethyl ether/85% pentane (V/V) and discard the eluate. This fraction will contain any diphenylamine.

10.2.4 Perform the second elution with 100 ml of 5% acetone/95% ethyl ether (V/V) and collect the eluate in a 500-ml K–D flask equipped with a 10-ml concentrator tube. This fraction will contain all of the nitrosamines.

10.2.5 Add 15 ml of methanol to the collected eluate and concentrate as in 9.5 at 70–75°C, substituting pentane for methylene chloride.

10.2.6 Analyze by gas chromatography.

10.3 Alumina Column Cleanup for Nitrosamines

10.3.1 Place 100g of alumina, as it comes from the manufacturer, into a 500 ml reagent bottle and add 2 ml of distilled water, which is free of nitrosamines and interferences. Mix the alumina preparation thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

10.3.2 Place 12 grams of the alumina preparation into a 10 mm ID chromatographic column and tap the column to settle the alumina. Add 1–2 cm of anhydrous sodium sulfate to the top of the alumina.

10.3.3 Preelute the column with 10 ml of 30% ethyl ether/70% pentane (V/V). Discard the eluate (about 2 ml) and, just prior to exposure of the sodium sulfate layer the air, transfer 2.0 ml of sample extract onto the column by decantation using an additional 2 ml of pentane to complete the transfer.

10.3.4 Just prior to exposure of the sodium sulfate layer to the air, add 70 ml of 30% ethyl ether/70% pentane. Discard the first 10 ml of eluate but collect the rest 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-nitrosodi-n-propylamine.

10.3.5 Next elute the column with 60 ml of 50% ethyl ether/50% pentane, collecting the eluate in a second K–D flask equipped with a 10 ml concentrator tube. Add 15 ml methyl alcohol to the K–D. This fraction will contain N-nitrosodimethylamine, most of the N-nitrosodi-n-propylamine and any diphenylamine.

10.3.6 Concentrate both fractions as in 9.5 substituting pentane for methylene chloride.

10.3.7 Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 N-nitrosodiphenylamine completely reacts to form diphenylamine at normal operating temperatures of the GC injection port. Therefore, N-nitrosodiphenylamine is actually chromatographed and detected as diphenylamine. The determination of either of the compounds in the original sample would be uncertain without the use of one of the previous cleanup procedures which separate the two compounds.

11.2 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.3 If the extract has not been submitted to one of the cleanup procedures in Section 10, it is necessary to exchange the solvent from methylene chloride to methyl alcohol before the thermionic detector can be used. To a 1–10 ml volume of methylene chloride extract in a concentrator tube, add 2 ml methyl alcohol, and a clean boiling chip. Attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a boiling water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position and insulate the apparatus as necessary 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 apparent volume of liquid reaches about 0.5 ml, remove the K-D and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of methyl alcohol. Adjust the final volume to 2.0 ml.

11.4 Inject 2–5 μl of the sample extract 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 units.

11.5 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.6 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)\,(V_s)}$$

Where:

A=Calibration factor for chromatographic system, in nanograms material per area unit.

B=Peak size in injection of sample extract, in area units

V_i=Volume of extract injected (μl)

V_t=Volume of total extract (μl)

V_s=Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 5—Nitrosamines," Report for EPA Contract 68–03–2606 (In preparation).

Table I.—Gas Chromatography of Nitrosamines

Nitrosamine	Retention time (min)		Detection limit (µg/l)[3]
	Col. 1[1]	Col. 2[2]	
N-nitrosodidimethylamine	4.1	0.88	0.3
N-nitrosodi-n-dipropylamine	12.1	4.2	0.5
N-nitrosodidiphenylamine	*12.8	**6.4	1.0

[1] Chromosorb WAW 80/100 mesh coated with 10% Carbowax 20M/2% KOH packed in a 180 cm long x 4 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Isothermal column temperature is 110°C except where * indicates 220°C.

[2] Supelcoport 100/120 mesh coated with 10% SP-2250 packed in a 180 cm long x 4 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Isothermal column temperature is 120°C except where ** indicates 210°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters. A nitrogren-phosphorus detector was used to collect this data, but a Thermal Energy Analyzer exhibited equivalent sensitivity.

BILLING CODE 6560-01-M

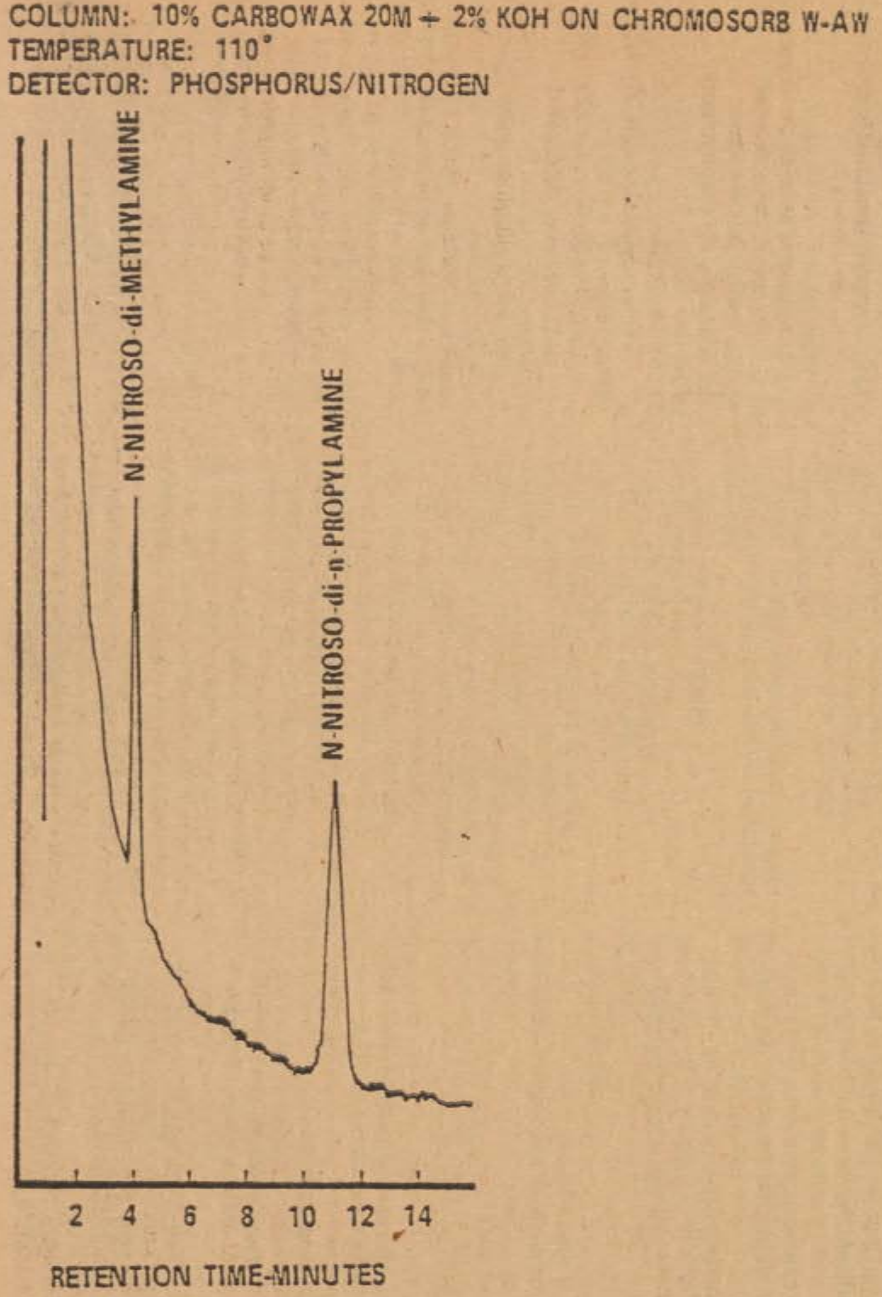

Figure 1. Gas chromatogram of nitrosamines

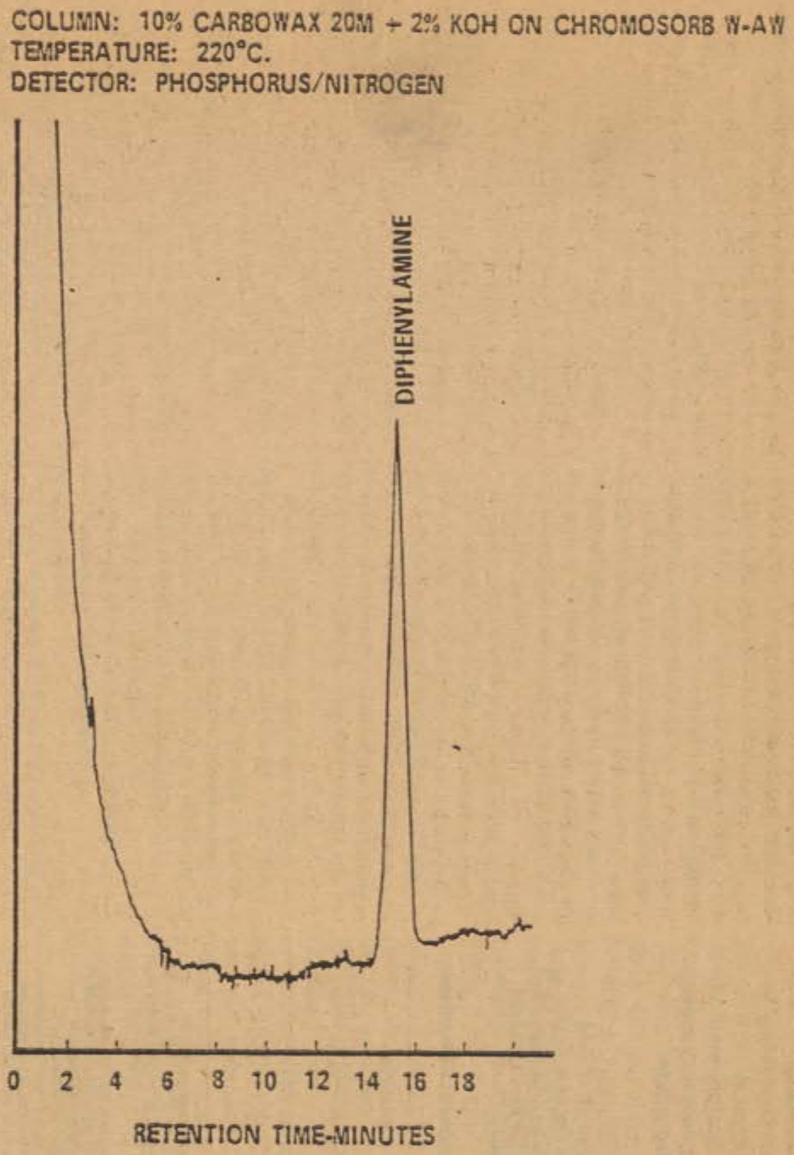

Figure 2. Gas chromatogram of N-nitrosodiphenylamine as diphenylamine

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Organochlorine Pesticides and PC3's—Method 608

1. *Scope and Application.*

1.1 This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs). The following parameters may be determined by this method:

Parameter:	Storet No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39259
g-BHC	39340
Chlordane	39350
4,4'-DDD	39310
4,4'-DDE	39320
4,4'-DDT	39300
Dieldrin	39380
Endosuflan I	34361
Endosuflan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with the use of a microcoulometric or electrolytic conductivity detector.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked at 1.0 and 10.0 ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Boiling chips—extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required acessories including electron capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—Pyrex, 400 mm × 25 mm OD, with coarse fritted plate and Teflon stopcock (Kontes K–42054–213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Boiling chips—Hengar granules (Hengar Co.; Fisher Co.) or equivalent.

5.6 Mercury—triple distilled.

5.7 Aluminum oxide—basic or neutral, active.

5.8 Hexane—pesticide residue analysis grade.

5.9 Isooctane (2,2,4-trimethyl pentane)—pesticide residue analysis grade.

5.10 Acetone—pesticide residue analysis grade.

5.11 Diethyl ether—Nanograde, redistilled in glass if necessary.

5.11.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y., 10523).

5.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.12 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch at least 16 hours at 130°C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 µg/l in the final extract, for example, prepare standards at 10 µg/l, 50 µg/l, 100 µg/l, 500 µg/l, etc., so that injections of 1–5 µl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 grams.

6.4 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must enploy 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, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 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. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. 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 sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 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.

10. *Cleanup and Separation.*

10.1 Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise disfigure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

10.2 Florisil Column Cleanup

10.2.1 Add a weight of Florisil, (nominally 21g.) predetermined by calibration (6.3, 6.4), to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1–2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

10.2.2 Adjust the sample extract volume to 10 ml and transfer it from the K–D concentrator tube to the Florisil column. Rinse the tube twice with 1–2 ml hexane, adding each rinse to the column.

10.2.3 Place a 500 ml K–D flask and clean concentrator tube under the chromatography 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 (Fraction 1) using a drip rate of about 5 ml/min. Remove the K–D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in nexane (Fraction 2), into a second K–D flask. Perform the third elution using 200 ml of 50% ethyl in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table II.

10.2.4 Concentrate the eluates by standard K–D techniques (9.5), substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

10.3 Elemental sulfur will usually elute entirely in Fraction 1. 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 1–3 drops of mercury and seal. Agitate the contents of the vial for 15–30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker and shake for 2 hours. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 through 10. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 µl of the sample extract 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 units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10–Pesticides and PCB's." Report for EPA Contract 68–03–2606.
2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I. —*Gas Chromatography of Pesticides and PCB's*

Parameter	Retention time (min) Col. 1 [1]	Col.2 [2]	Detection limit (µg/1) [3]
Aldrin	2.40	4.10	0.003
a-BHC	1.35	1.82	0.002
b-BHC	1.90	1.97	0.004
d-BHC	2.15	2.20	0.004
g-BHC	1.70	2.13	0.002
Chlordane	(4)	(4)	0.04
4,4†-DDD	7.83	9.08	0.012
4,4†-DDE	5.13	7.15	0.006
4,4†-DDT	9.40	11.75	0.016
Dieldrin	5.45	7.23	0.006
Endosulfan I	4.50	6.20	0.005
Endosulfan II	8.00	8.28	0.01
Endosulfan sulfate	14.22	10.70	0.03
Endrin	6.55	8.10	0.009
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.002
Heptachlor epoxide	3.50	5.00	0.004
Toxaphene	(4)	(4)	0.40
PCB-1016	(4)	(4)	0.04
PCB-1221	(4)	(4)	0.10
PCB-1232	(4)	(4)	0.10
PCB-1242	(4)	(4)	0.05
PCB-1248	(4)	(4)	0.08
PCB-1254	(4)	(4)	0.08
PCB-1260	(4)	(4)	0.15

[1] Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[2] Supelcoport 100/120 mesh coated with 3% OV-1 in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

[4] Multiple peak response. See Figures 2–10.

Table II. —*Distribution and Recovery of Chlorinated Pesticides and PCBs Using Florisil Column Chromatography*

Parameter	Recovery (percent) by fraction [1]		
	1(6 pct.)	2 (15 pct.)	3 (50 pct.)
Aldrin	100		
a-BHC	100		
b-BHC	97		
d-BHC	98		
g-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4c4'-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		

[1] From: "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10-Pesticides and PCB's. Report for EPA Contract 68-03-2606."

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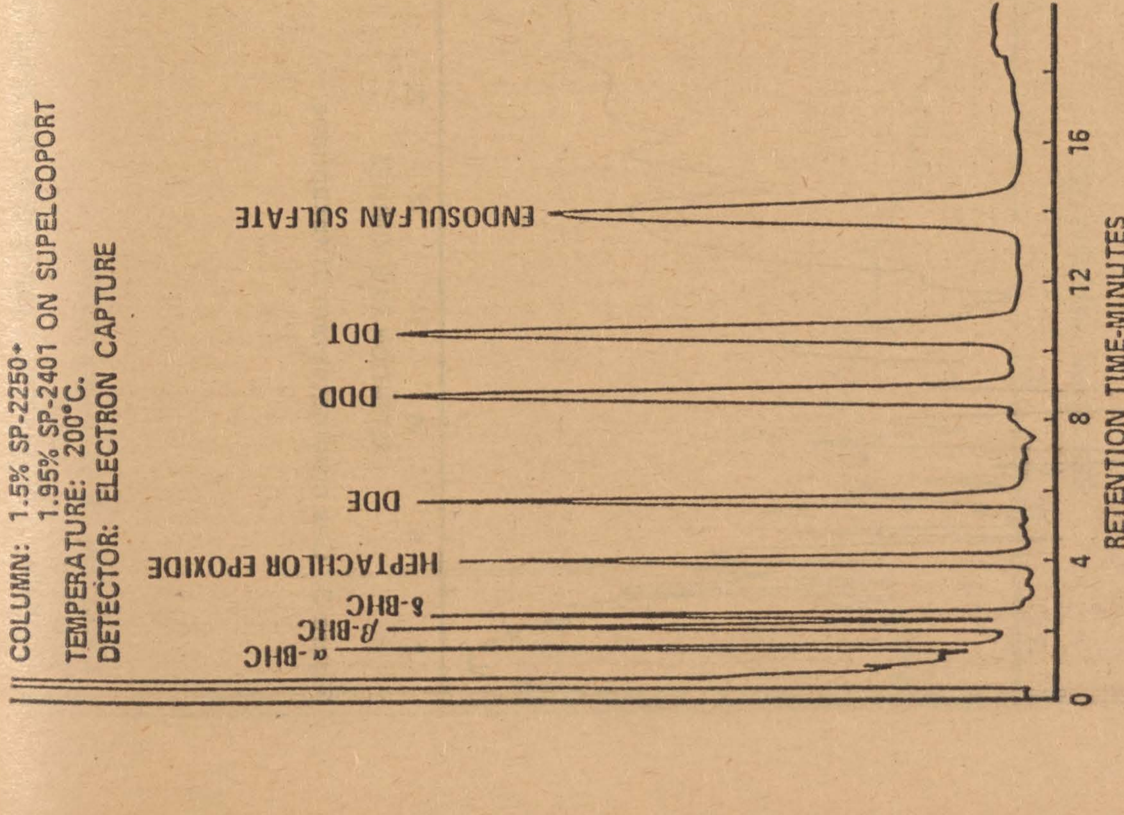

Figure 1. Gas chromatogram of pesticides

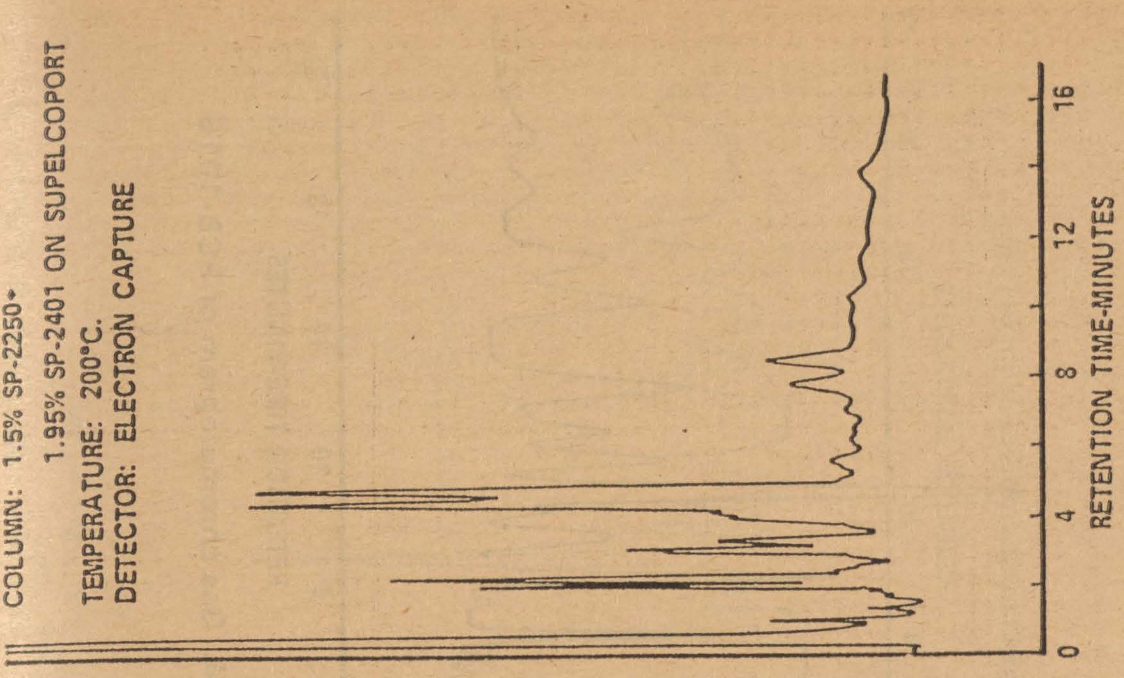

Figure 2. Gas chromatogram of chlordane

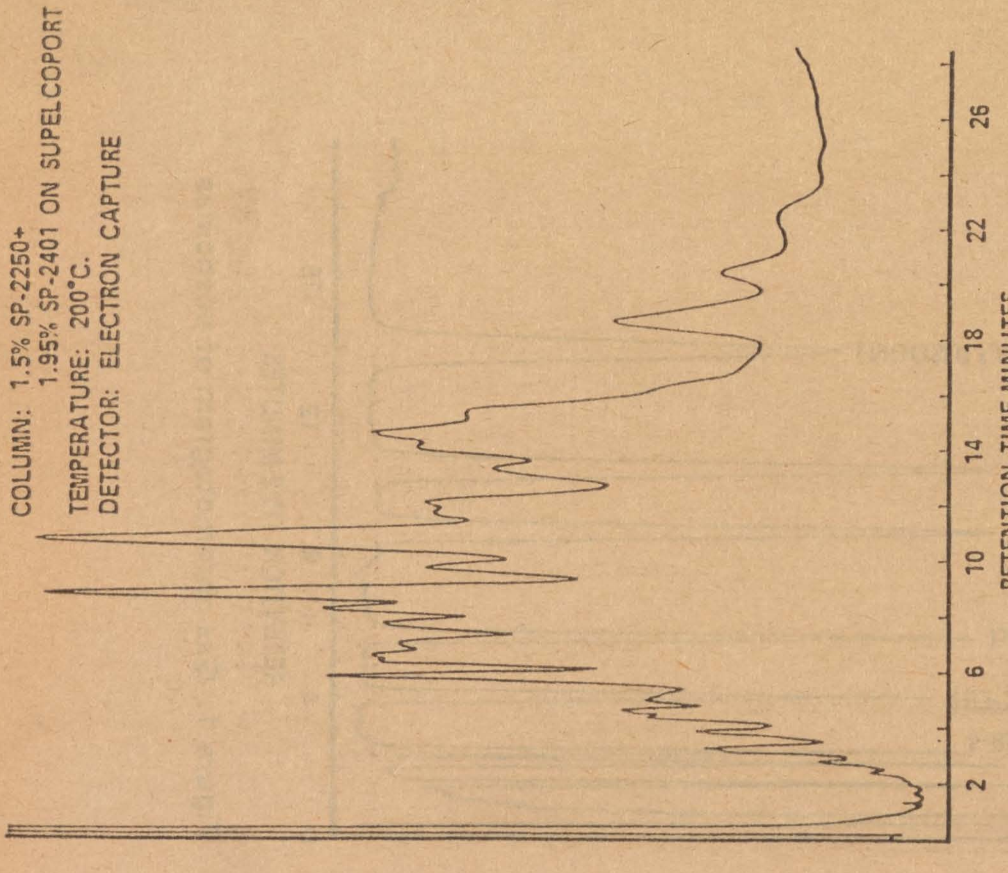

Figure 3. Gas chromatogram of toxaphene

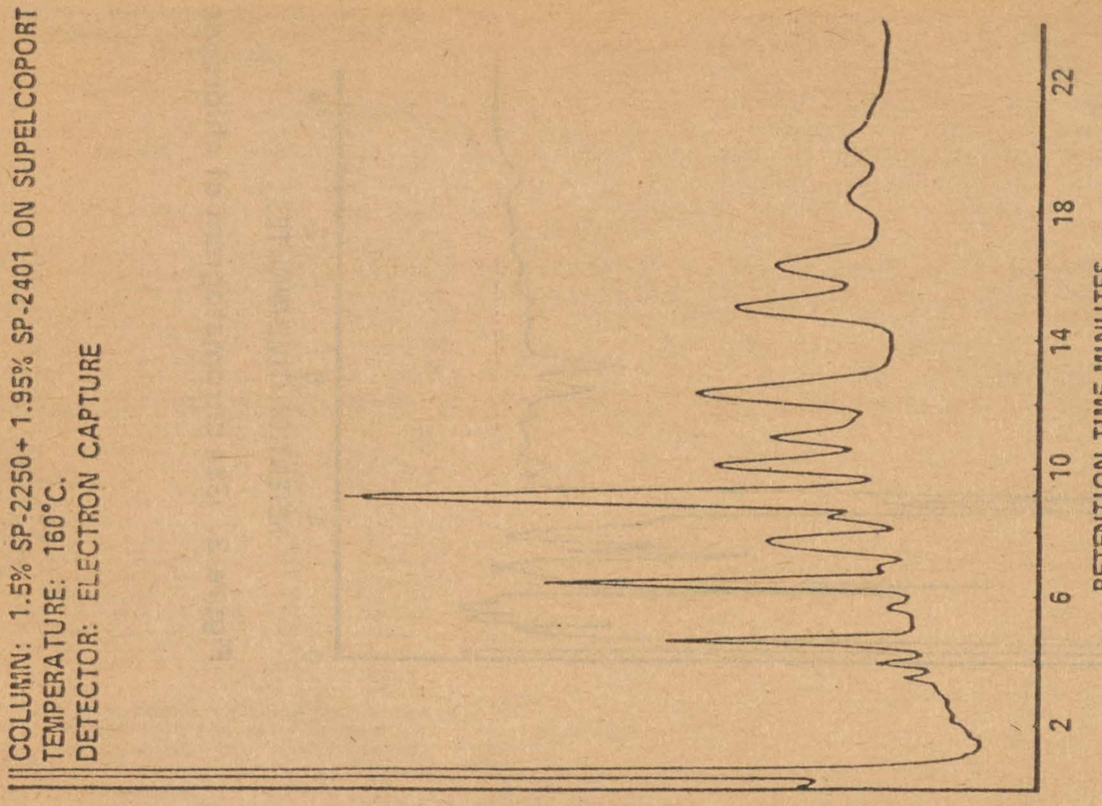

Figure 4. Gas chromatogram of PCB-1016

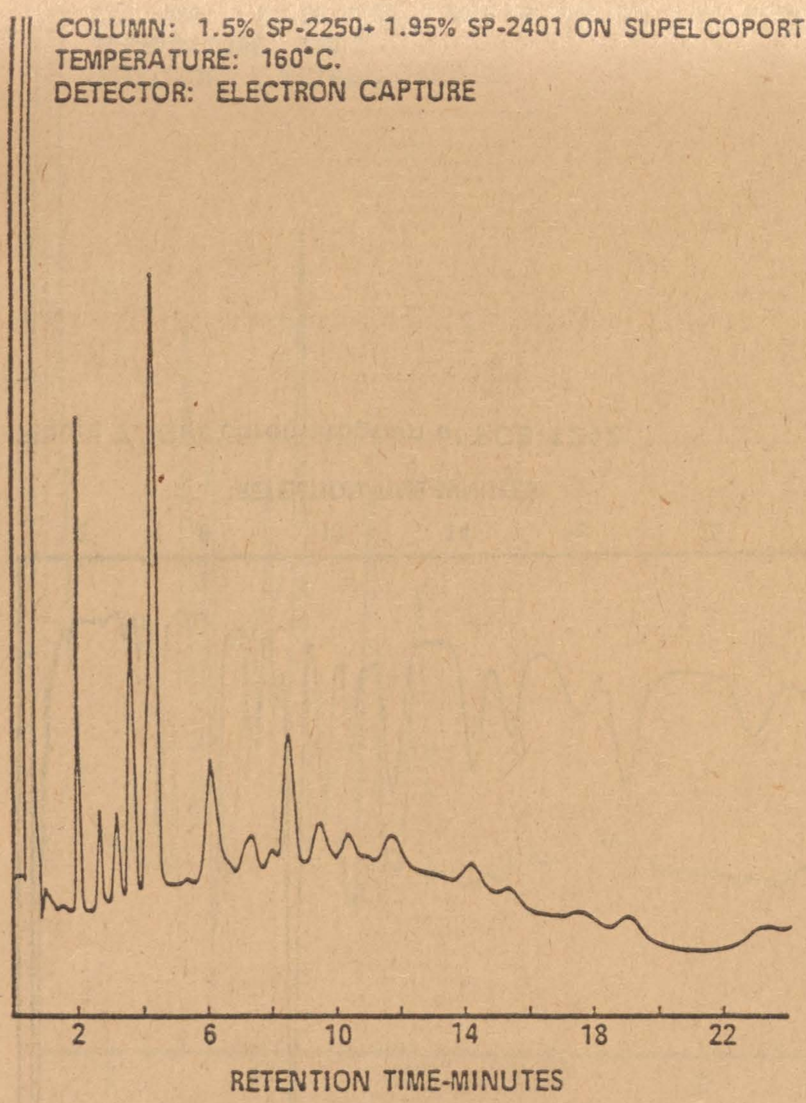

Figure 5. Gas chromatogram of PCB-1221

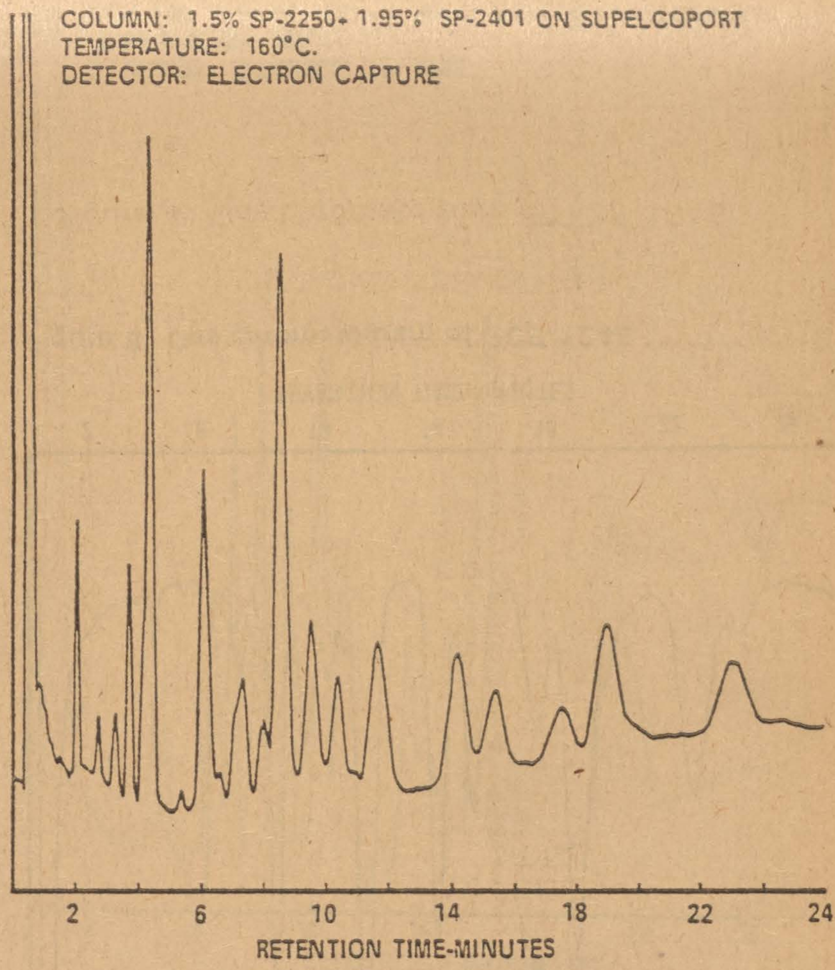

Figure 6. Gas chromatogram of PCB-1232

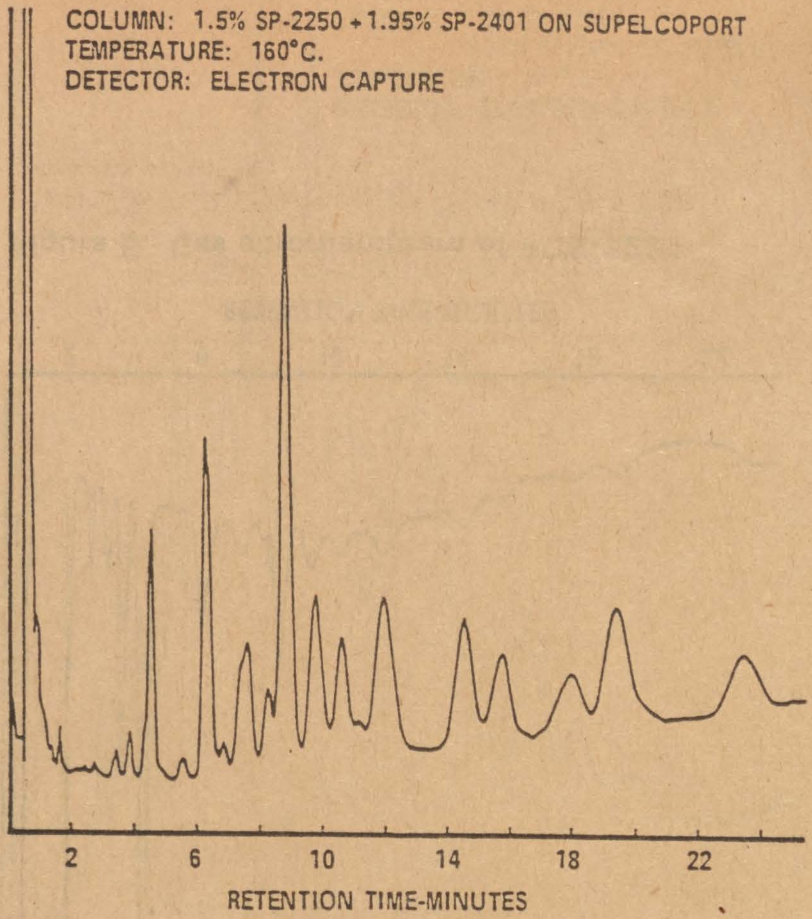

Figure 7. Gas chromatogram of PCB-1242

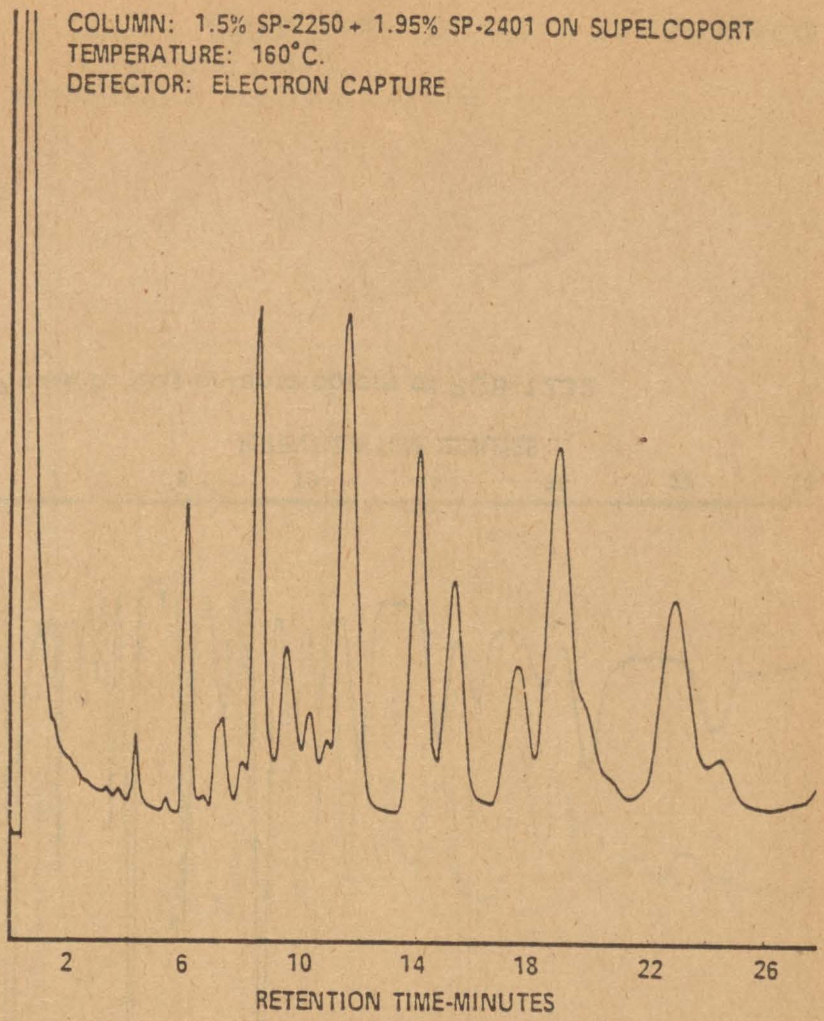

Figure 8. Gas chromatogram of PCB-1248

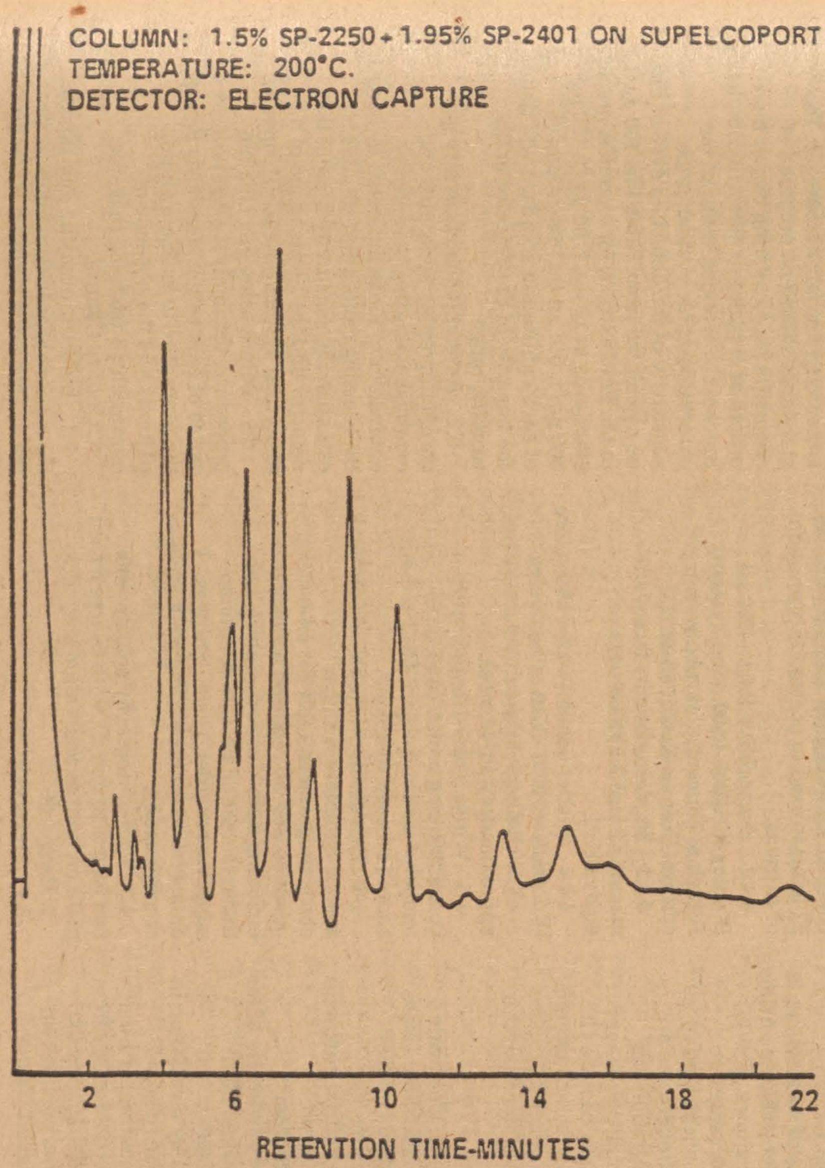

Figure 9. Gas chromatogram of PCB-1254

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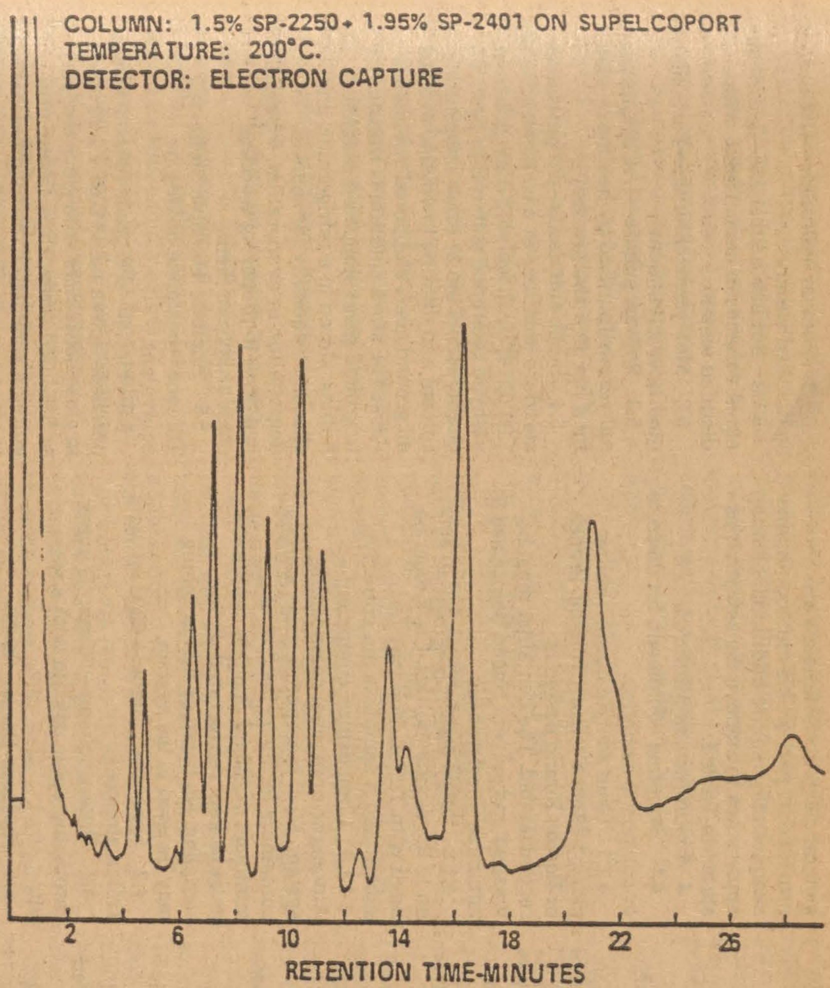

Figure 10. Gas chromatogram of PCB-1260

Nitroaromatics and Isophorone—Method 609

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.*
Isophorone	34408
Nitrobenzene	34447
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharege Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compunds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and exchanged to toluene while being concentrated to 1.0 ml. Isophorone and nitrobenzene are measured by flame ionization gas chromatography. The dinitrotoluenes are measured by electron capture GC.

2.2 If interferences are encountered, the method provides a general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569001–0219 or equivalent).

4.4.5 Boiling chips-solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including both electron capture and flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—400 mm long x 10 mm ID, with coarse fritted plate on bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetone, Haxane, Methanol, Toluene—pesticide quality or equivalent.

5.6 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 200°C in glass containers loosely covered with foil.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/1 in the final extract, for example, prepare standards at 10 μg/1, 50 μg/1, 100 μg/1, 500 μg/1, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techiques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. 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.

9.6 Add 1.0 ml toluene to the concentrator tube, and a clean boiling chip. 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 this micro-K–D apparatus on a water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. 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 for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of toluene. Adjust the final volume to 1.0 ml and stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. Unless the sample is known to require cleanup, proceed with gas chromatographic analysis.

9.7 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.

10. *Cleanup and Separation.*

10.1 Prepare a slurry of 10g of activated Florisil in 10% methylene chloride in hexane (V/V). Use it to pack a 10 mm ID chromatography column, gently tapping the column to settle the Florisil. Add 1 cm anhydrous sodium sulfate to the top of the Florisil.

10.1.1 Just prior to exposure of the sodium sulfate layer to the air transfer the 1 ml sample extract onto the column using an additional 2 ml of toluene to complete the transfer.

10.1.2 Just prior to exposure of the sodium sulfate layer to the air, add 30 ml 10% methylene chloride in hexane and continue the elution of the column. Elution of the column should be at a rate of about 2 ml per minute. Discard the eluate from this fraction.

10.1.3 Next elute the column with 30 ml of 10% acetone/90% methylene chloride (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Concentrate the collected fraction by the K–D technique prescribed in 9.5 and 9.6, including the solvent exchange to 1 ml toluene. This fraction should contain the nitroaromatics and isophorone.

10.1.4 Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Isophorone and nitrobenzene are analyzed by injection of a portion of the extract into a gas chromatograph with a flame ionization detector. The dinitrotoluenes are analyzed by a separate injection into an electron capture gas chromatograph. Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instruments. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract 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 units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.
B = Peak size in injection of sample extract, in area units.
V_i = Volume of extract injected (µl).
V_t = Volume of total extract (µl).
V_s = Volume of water extracted (ml).

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4-Nitroaromatics and Isophorone," Report for EPA Contract No. 68–03–2624 (In preparation).

Table I. —*Gas Chromatography of Nitroaromatics and Isophorone*

Compound	Retention time (min.)		Detection limit (µg/l)[3]	
	Col. 1[1]	Col. 2[2]	EC	FID
Isophorone	4.49	5.72	....	5
Nitrobenzene	3.31	4.31	....	5
2,4-Dinitrotoluene	5.35	6.54	0.06	....
2,6-Dinitrotoluene	3.52	4.75	0.06	....

[1] Gas-Chrom Q 80/100 mesh coated with 1.95% OF-1/1.5% OV-17 packed in a 4′ × ¼″ OD glass column. FID analysis for IP and NB requires nitrogen caier gas at 44 ml/min and 85°C column temperature. EC analysis for the DNTs requires 10% Methane/90% Argon carrier gas at 44 ml/min flow rate and 145°C column temperature.

[2] Gas-Chrom Q 80/100 mesh coated with 3% OV–101 packed in a 10′ × ¼″ OD glass column. FID analysis of IP and NB requires nitrogen carrier gas at 44 ml/min flow rate and 100°C column temperature. EC analysis for the DNTs requires 10% Methane/90% Argon carrier gas at 44 ml/min flow rate and 150°C column temperature.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microfliters.

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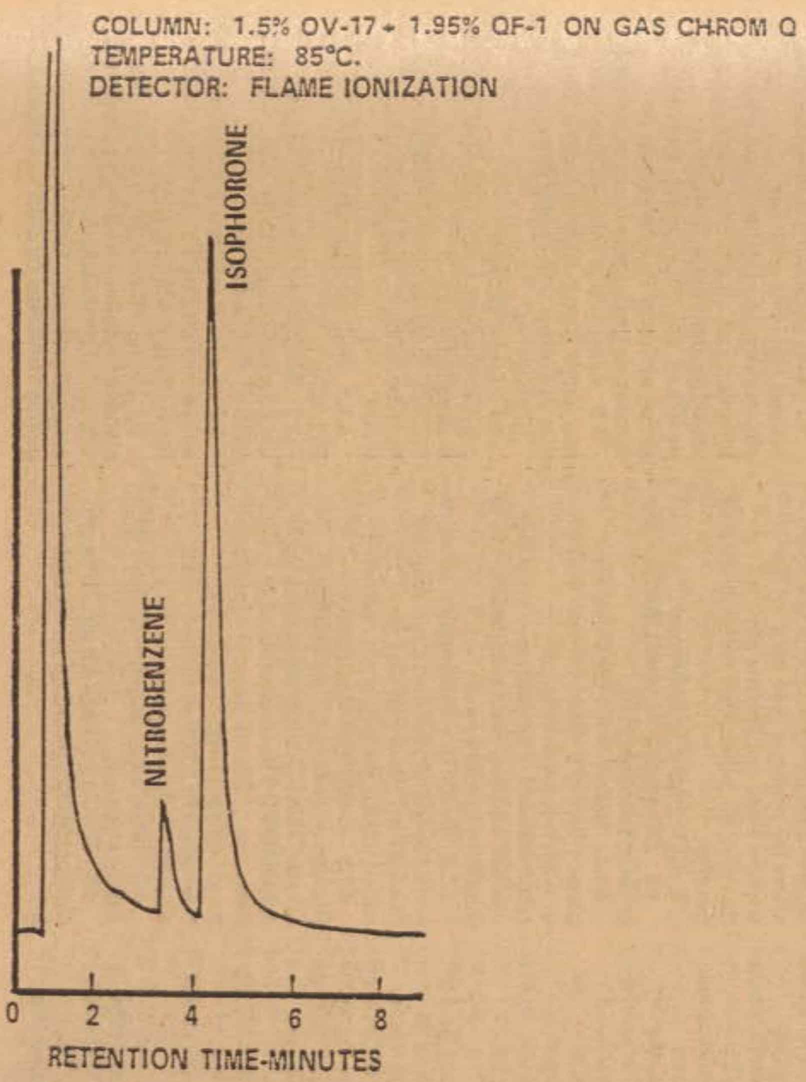

Figure 1. Gas chromatogram of nitrobenzene and isophorone

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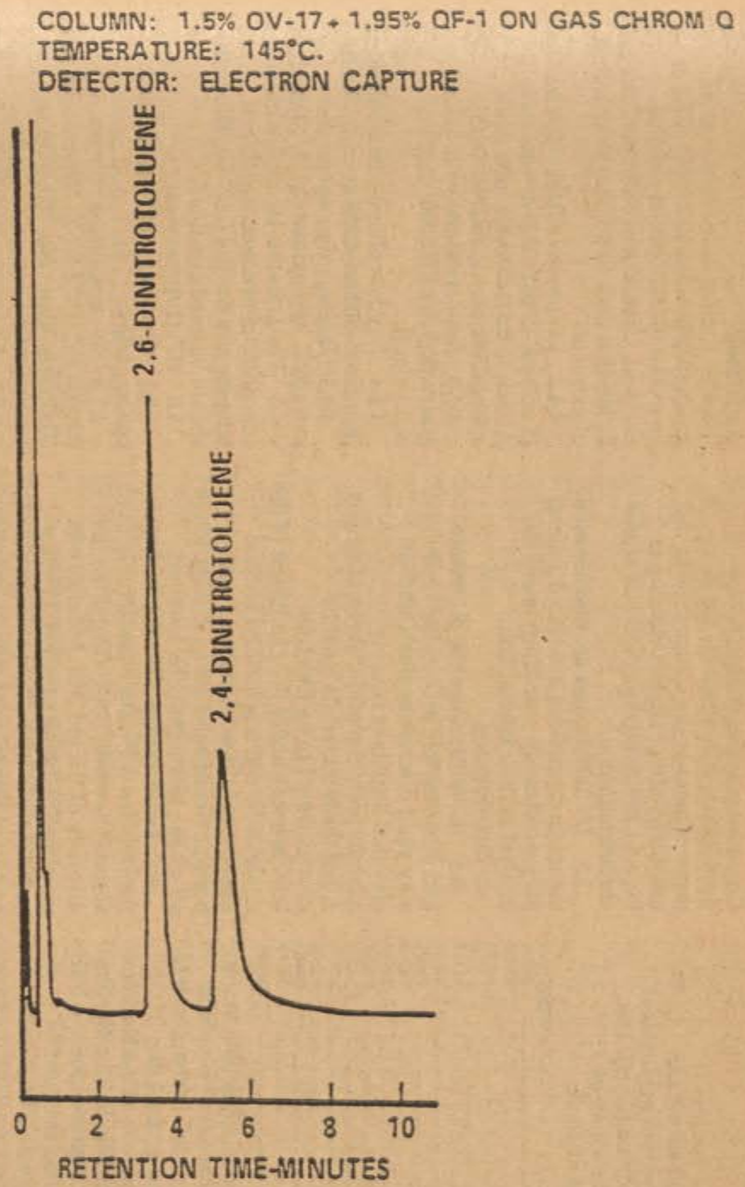

Figure 2. Gas chromatogram of dinitrotoluenes

Polynuclear Aromatic Hydrocarbons—Method 610

1. *Scope and Application.*

1.1 This method covers the determination of certain polynuclear aromatic hydrocarbons (PAH). The following parameters may be determined by this method:

Parameter:	*STORET No.*
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(a)pyrene	34247
Benzo(b)fluoranthene	34230
Benzo(ghi)perylene	34521
Benzo(k)fluoranthene	34242
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Fluoranthene	34376
Fluorene	34381
Indeno(1,2,3-cd)pyrene	34403
Nephthalene	34696
Phenanthrene	34461
Pyrene	34469

1.2 This method is applicable to the determination of these compounds in muncipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 This method contains both liquid and gas chromatographic approaches, depending upon the needs of the analyst. The gas chromatographic procedure cannot 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 purposes of the analysis can be served by reporting a sum for an unresolved pair, the liquid chromatographic approach must be used for these compounds. The liquid chromatographic method will resolve all of the 16 compounds listed above.

1.4 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I for the liquid chromatographic approach represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.5 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract by either High Performance Liquid Chromatography (HPLC) or gas chromatography.

2.2 If interferences are encountered, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While a general clean-up technique is provided as part of this method, unique samples may require additional clean-up approaches to acheive the sensitivities stated in Table 1.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontex K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 HPLC Apparatus:

4.6.1 Gradient pumping system, constant flow.

4.6.2 Reverse phase column, 5 micron HC-ODS Sil-X, 250 mm × 2.6 mm ID (Perkin Elmer No. 809-0716 or equivalent).

4.6.3 Fluorescence detector, for excitation at 280 nm and emission at 389 nm.

4.6.4 UV detector, 254 nm, coupled to fluorescence detector.

4.6.5 Strip chart recorder compatible with detectors, (A data system for measuring peak areas is recommended).

4.7 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including dual flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.8 Chromatographic column—250 mm long × 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Methylene chloride, Pentane, Cyclohexane, High Purity Water—HPLC quality, distilled in glass.

5.3 Sodium sulfate—(ACS) Granular, anhydrous (purified by heating at 400° C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 $\mu g/\mu l$ by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetonitrile—Spectral quality.

5.6 Silica gel—100/120 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hours at 130° C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary HPLC or gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I or II. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

6.3 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as fraction collection and GC-mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, adjust the sample to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid and add 35 mg sodium thiosulfate per part per million of free chlorine per liter.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a munimum of ten minutes. If the emulsion inteface between layers is more than one-third the size 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, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10-ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30-ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1-ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparatus volumn of liquid reaches 1-ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. 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. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.6 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.

9.7 If the sample requires cleanup before chromatographic analysis, proceed to Section 10. If the sample does not require cleanup, or if the need for cleanup is unkown, analyze an aliquot of the extract according to Section 11 or Section 12.

10. *Cleanup and Separation.*

10.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1–10-ml aliquot of sample extract (in methylene chloride) and a boiling chip to a clean K–D concentrator tube. Add 4-ml cyclohexane and attach a micro-Snyder column. Prewet the micro-Snyder column by adding 0.5-ml 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 5–10 minutes. 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 K–D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane. Adjust the extract volume to about 2-ml.

10.2 Silica Gel Column Cleanup for PAHs.

10.2.1 Prepare a slurry of 10g activated silical gel in methylene chloride and place this in a 10 mm ID chromatography column. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1–2 cm of anhydrous sodium sulfate to the top of the silica gel.

10.2.2 Preelute the column with 40-ml pentane. 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 of cyclohexane to complete the transfer.

10.2.3 Just prior to exposure of the sodium sulfate layer to the air, add 25-ml pentane and continue elution of the column. Discard the pentane eluate.

10.2.4 Elute the column with 25-ml of 40% methylene chloride/60% pentane and collect the eluate in a 500-ml K–D flask equipped with a 10-ml concentrator tube. Elution of the column should be at a rate of about 2 ml/min.

10.2.5 Concentrate the collected fraction to less than 10-ml by K–D techniques as in 9.5, using pentane to rinse the walls of the glassware. Proceed with HPLC or gas chromatographic analysis.

11. *High Performance Liquid Chromatography HPLC.*

11.1 To the extract in the concentrator tube, add 4 ml acetonitrile and a new boiling chip, then attach a micro-Snyder column. Increase the temperature of the hot water bath to 95–100° C. Concentrate the solvent as above. After cooling, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 ml acetonitrile. Adjust the extract volume to 1.0 ml.

11.2 Table I summarizes the recommended HPLC column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 1. Calibrate the system daily with a minimum of three injections of calibration standards.

11.3 Inject 2–5 μl of the sample extract with a high pressure syringe or sample injection loop. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.5 If the peak area measurement is prevented by the pressure of interference, further cleanup is required.

11.6 The UV detector is recommended for the determination of napthalene and acenaphthylene and the fluorescene detector is recommended for the remaining PAHs.

12. *Gas Chromatography.*

12.1 The gas chromatographic procedure will not resolve certain isomeric pairs as indicated in Table II. The liquid chromatographic procedure (Section 11) must be used for these materials.

12.2 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 this micro-K-D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. 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 for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 ml and stopper the concentrator tube.

12.3 Table II describes the recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times that should be achieved by this method. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.

12.4 Inject 2–5 μl of the sample extract 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 ara units.

12.5 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 If the peak ara measurement is prevented by the presence of interferences, further cleanup is required.

13. *Calculations.*

13.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/1} = \frac{(A)\,(B)\,(V_t)}{(V_i)\,(V_s)}$$

Where:

A=Calibration factor for chromatographic system, in nanograms material per area unit.

B=Peak size in injection of sample extract, in area units

V_i=Volume of extract injected (μl)

V_t=Volume of total extract (μl)

V_s=Volume of water extracted (ml)

13.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14. *Accuracy and Precision.*

14.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 9-PAHs." Report for EPA Contract 68–03–2624 (In preparation).

Table I.—*High Performance Liquid Chromatography of PAH's*

Compound [1]	Retention time (min)	Detection limit (μg/l) [2]	
		UV	Fluorescence
Naphthalene	16.17	2.5	20.0
Acenaphthylene	18.10	5.0	100.0
Acenaphthene	20.14	3.0	4.0
Fluorene	20.89	0.5	2.0
Phenanthrene	22.32	0.25	1.2
Anthracene	23.78	0.10	1.5
Fluoranthene	25.00	0.50	0.05
Pyrene	25.94	0.10	0.05
Benzo(a)anthracene	29.26	0.20	0.04
Chrysene	30.14	0.20	0.5
Benzo(b)fluoranthene	32.44	1.0	0.04
Benzo(k)fluoranthene	33.91	0.30	0.04
Benzo(a)pyrene	34.95	0.25	0.04
Dibenzo(a,h)anthracene	37.06	1.0	0.08
Benzo(ghi)perylene	37.82	0.75	0.2
Indeno(1,2,3-cd)pyrene	39.21	0.30	0.1

[1] HPLC conditions: Reverse phase HC-ODS Sil-X 2.6 × 250 mm Perkin-Elmer column; isocratic elution for 5 min. using 40% acetonitrile/60% water, then linear gradient elution to 100% acetonitrile over 25 minutes; flow rate is 0.5 ml/min.

[2] Detection limit is calculated from the minimum detectable HPLC response being equal to five times the background noise, assuming an equivalent of a 2 ml final volume of the 1 liter sample extract, and assuming an HPLC injection of 2 microliters.

Table II.—*Gas Chromatography of PAHs*

Compound [1]	Retention Time (min)
Naphthalene	4.5
Acenaphthylene	10.4
Acenaphthene	10.8
Fluorene	12.6

Table II.—*Gas Chromatography of PAHs*—Continued

Compound [1]	Retention Time (min)
Phenanthrene	15.9
Anthracene	15.9
Fluoranthene	19.8
Pyrene	20.6
Benzo(a)anthracene	20.6
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

[1] GC conditions: Chromosorb W-AW-DCMs 100/120 mesh coated with 3% OV-17, packed in a 6′ x 2 mm ID glass column, with nitrogen carrier gas at 40 ml/min flow rate. Column temperature was held at 100° C for 4 minutes, then programmed at 8°/minute to a final hold at 280° C.

Haloethers—Method 611

1. *Scope and Application*

1.1 This method covers the determination of certain haloethers. The following parameters may be determined by this method:

Parameter:	STORET No.
Bis(2-chloroethyl) ether	34273
Bis(2-chloroethoxy) methane	34278
Bis(2-chloroisopropyl) ether	34283
4-Bromophenyl phenyl ether	34636
4-Chlorophenyl phenyl ether	34641

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions utilizing a halide specific detector are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides a selected general

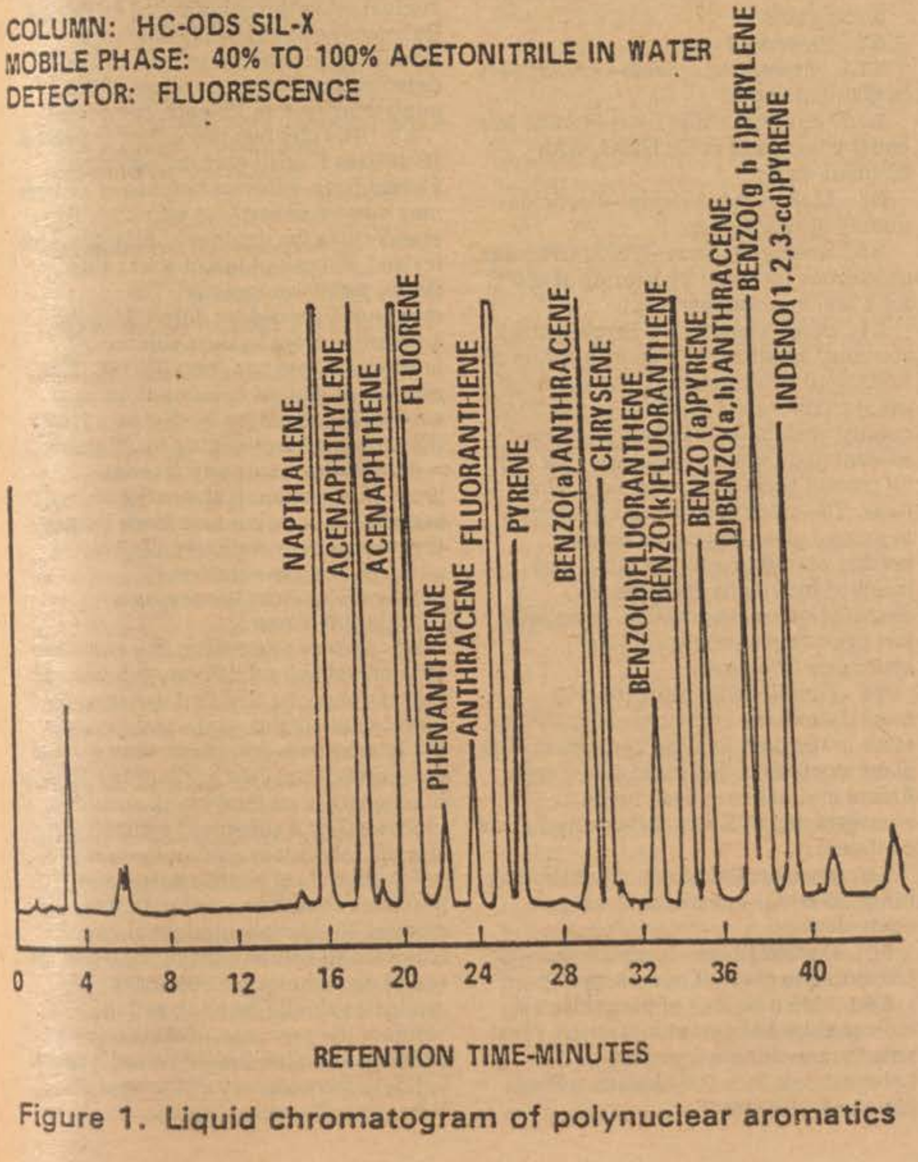

Figure 1. Liquid chromatogram of polynuclear aromatics

purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artificats and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

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. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample in not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size $^{19}/_{22}$ joint) is used to prevent ecaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569001–0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately $^{10}/_{40}$ mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including halide specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic Column—400 mm long x 19 mm ID with coarse fritted plate on bottom and Teflon stopcock (Kontes K–420540–0224 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality acetone or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Florisil—PR Grade (60/100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in a foil-covered glass container.

5.6 Hexane, Petroleum ether (boiling range 30–60°C)—pesticide quality or equivalent.

5.7 Diethyl Ether—Nanograde, redistilled in glass, if necessary.

5.7.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.7.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 grams.

6.4 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size 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, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1–2 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

Note.—Haloethers have a sufficiently high volatility that 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 1–2 ml before removing the K–D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85–90°C. Concentrate the extract as in 9.5 except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.7 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.

9.8 Unless the sample is known to require cleanup, proceed to analysis by gas chromatography.

10. *Cleanup and Separation.*

10.1 Florisil Column Cleanup for Haloethers.

10.1.1 Adjust the sample extract volume to 10 ml.

10.1.2 Place a charge (nominally 20 g but determined in Section 6.3) of activated Florisil in a 19 mm ID chromatography column. After settling the Florisil by tapping column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 50–60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into 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 6% ethyl ether/94% petroleum ether. 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.

10.1.4 Concentrate the fraction by K–D as in 9.5 except prewet the Snyder column with hexane. When the apparatus is cool, remove the column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 µl of the sample extract 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 units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = volume of extract injected (µl)

V_t = volume of total extract (µl)

V_s = volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 2-Haloethers." Report for EPA Contract 68–03–2633 (In preparation).

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I.—*Gas Chromatography of Haloethers*

Compound	Retention time (min.)		Detection limit (ug/L)[3]
	Col. 1[1]	Col. 2[2]	
Bis(2-chloroisopropyl) ether	8.41	9.70	0.9
Bis(2-chloroethyl) ether	9.32	9.06	0.5
Bis(2-chloroethoxy) methane	13.1	9.97	0.4
4-Chlorophenyl phenyl ether	19.4	15.0	2.2
4-Bromophenyl phenyl ether	21.2	16.2	1.1

[1] Supelcoport 100/120 mesh coated with 3% SP-1000 packed in 1.8 m long x 2.1 mm ID glass column with ultra-high purity helium carrier/gas at 40 ml/min flow rate. Column temperature is 60°C for 2 minutes after injection then program at 8°C/min to 230°C and hold for 4 minutes. Under these conditions R.T. of Aldrin is 22.6 minutes.

[2] Tenax-GC 60/80 mesh packed in a 1.8 m long x 2.1 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Column temperature 150°C for 4 minutes after injection then program at 16°C/min to 310°C. Under these conditions R.T. of Aldrin is 18.4 minutes.

[3] Detection is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a FC injection of 5 microliters. These values were collected using the Tracor 700 Hall electrolytic conductivity detector with furnace temperature 900°C, transfer line 250°C, 95% ethanol electrolyte at 0.3 ml/min flow rate, and hydrogen reaction gas at 60 ml/min.

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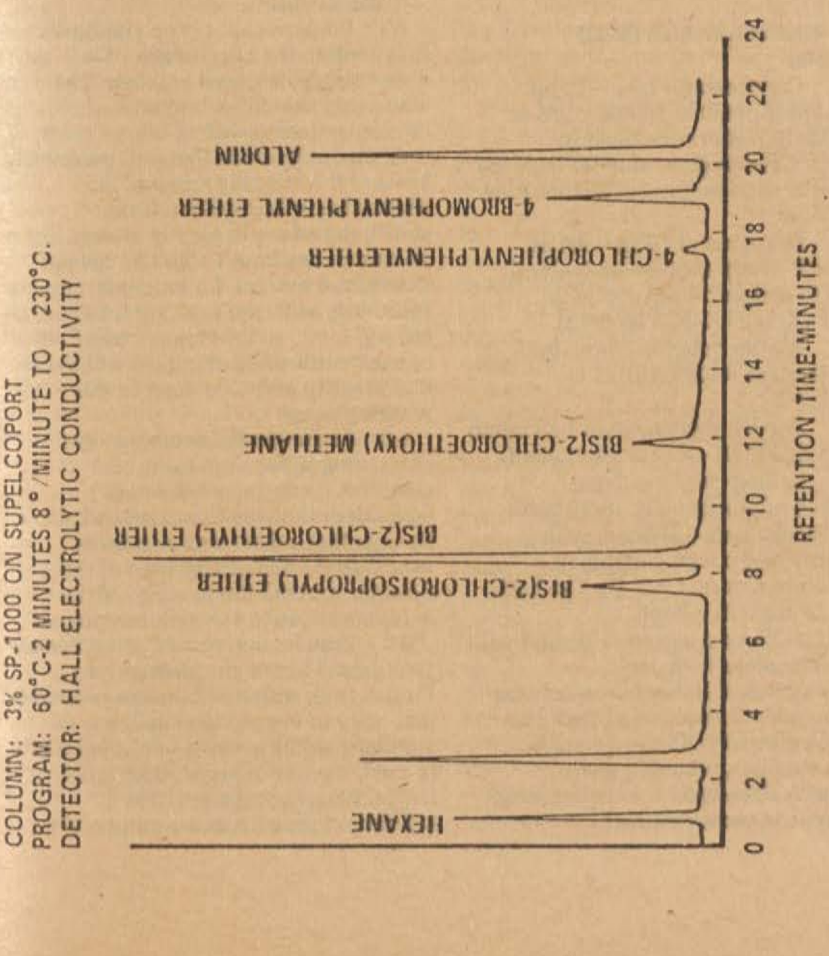

Figure 1. Gas chromatogram of haloethers

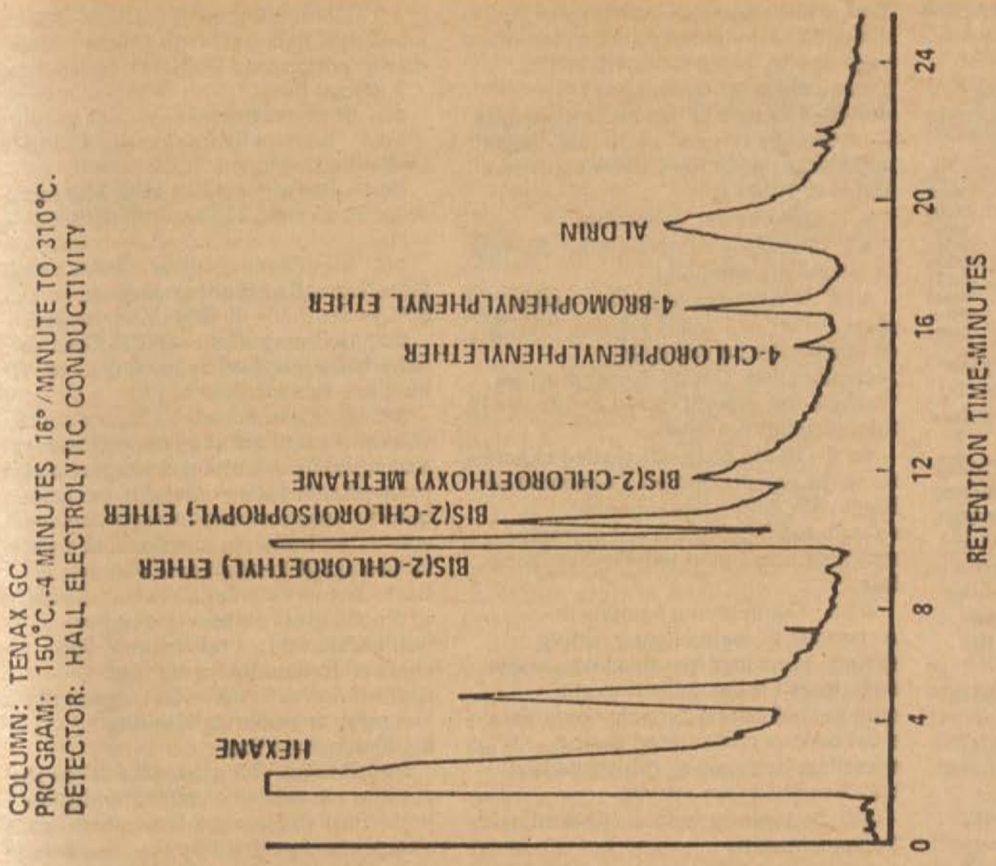

Figure 2. Gas chromatogram of haloethers

Chlorinated Hydrocarbons—Method 612

1. *Scope and Application.*

1.1 This method covers the determination of certain chlorinated hydrocarbons. The following parameters may be determined by this method.

Parameter:	*STORET No.*
Hexachlorocyclopentadiene	34386
Hexachlorobenzne	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
1,2-Dichlorobenzene	34536
1,2,4-Drichlorobenzene	34551
1,3-Dichlorobenzene	34566
1,4-Dichiorobenzene	34571
2-chloronaphthalene	34581

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is ususally dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of inteferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried by passing through a sodium sulfate column and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If inteferences are encountered or expected, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from inteferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities states in Table 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1 2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive and the foil is found to be interference free.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569001–0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—300 mm long × 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride, Hexane and Petroleum ether (boiling range 30–60°C)—Pesticide quality or equivalent.

5.3 Sodium sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at 130°C in foil-covered glass containers.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/1 in the final extract, for example, prepare standards at 10 μg/1, 50 μg/1, 100 μg/1, 500 μg/1, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this ratio by 110 and multiplying by 20 grams.

6.4 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers, leaving a minimum headspace. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples should be extracted immediately and must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size 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, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1–2 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

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 1–2 ml before removing the K-D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85–90° C. Concentrate the extract as in 9.5, except using hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 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.

9.7 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.

9.8 Unless the sample is known to require cleanup, proceed to analysis by gas chromatography.

10. *Cleanup and Separation.*

10.1 Florisil column cleanup for chlorinated Hydro-carbons.

10.1.1 Adjust the sample extract to 10 ml.

10.1.2 Place a 12 gram charge of activated Florisil (see 6.3) in a 10 mm ID chromatography column. After settling the Florisil by tapping the column, add a 1–2 cm layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 100 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into 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 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.

10.1.4 Concentrate the fraction by K–D as in 9.5 except prewet the column with hexane. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes the recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by this column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.
B = Peak size in injection of sample extract, in area units
V_i = Volume of extract injected (ul)
V_t = Volume of total extract (ul)
V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3—Chlorinated Hydrocarbons and Category 8—Phenols." Report for EPA Contract 68-03-2625 (In preparation).

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, *29* (1968).

Table I.—*Gas Chromatography of Chlorinated Hydrocarbons*

Compound	Retention time (min.) col. 1[1]	Detection limit (μg/l)[2]
1,3-dichlorobenzene	4.0	0.009
1,4-dichlorobenzene	4.3	0.018
Hexachloroethane	4.8	0.001
1,2-dichlorobenzene	5.3	0.012
Hexachlorobutadiene	11.6	0.001
1,2,4-trichlorobenzene	12.4	0.006
Hexachlorocyclopentadiene	*1.5	0.001
2-chloronaphthalene	*2.5	0.015
Hexachlorobenzene	*7.0	0.001

[1] Gas Chrom Q 80/100 mesh coated with 1.5% OV-1/1.5% OV-225 packed in a 1.8 m long x 2 mm ID glass column with 5% Methane/95% Argon carrier gas at 30 ml/min flow rate. Column temperature is 75° C except where * indicates 160° C. Under these conditions R.T. of Aldrin is 18.8 minutes at 160° C.

[2] Detection limit is calculated from the minimum detectable GC response of the electron capture detector being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

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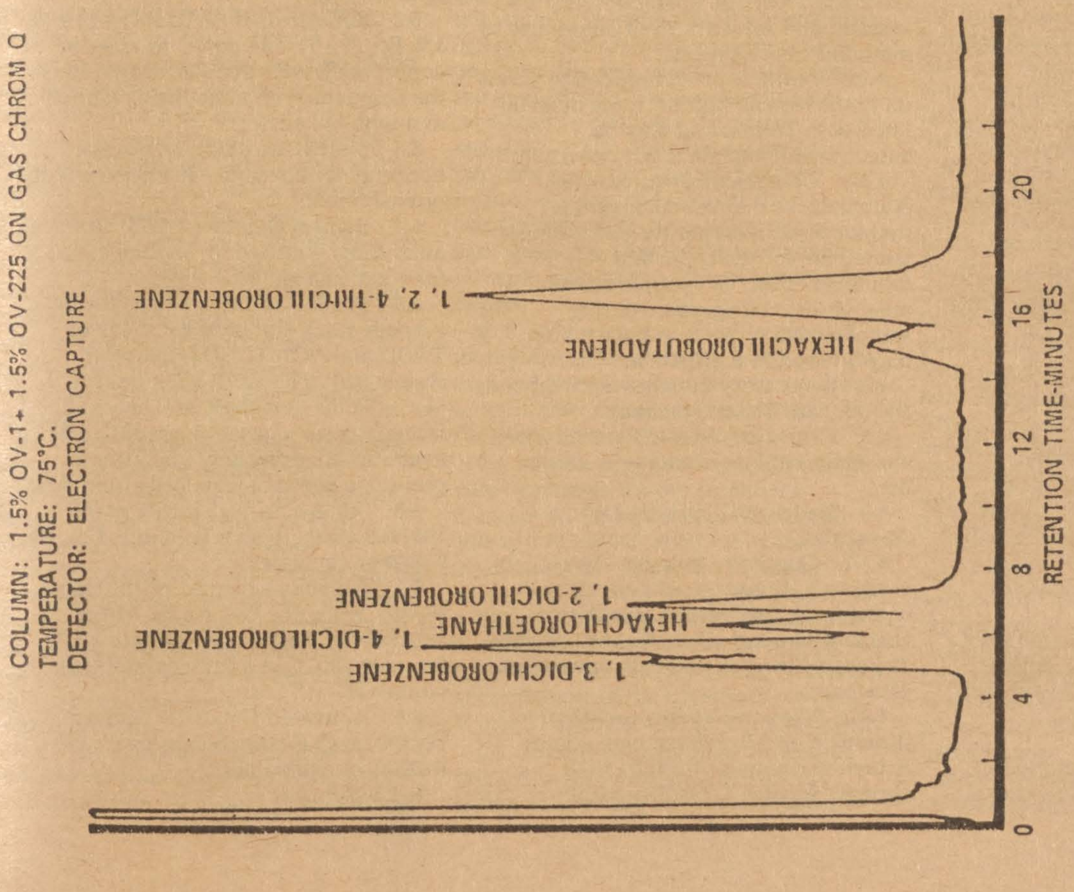

Figure 1. Gas chromatogram of chlorinated hydrocarbons

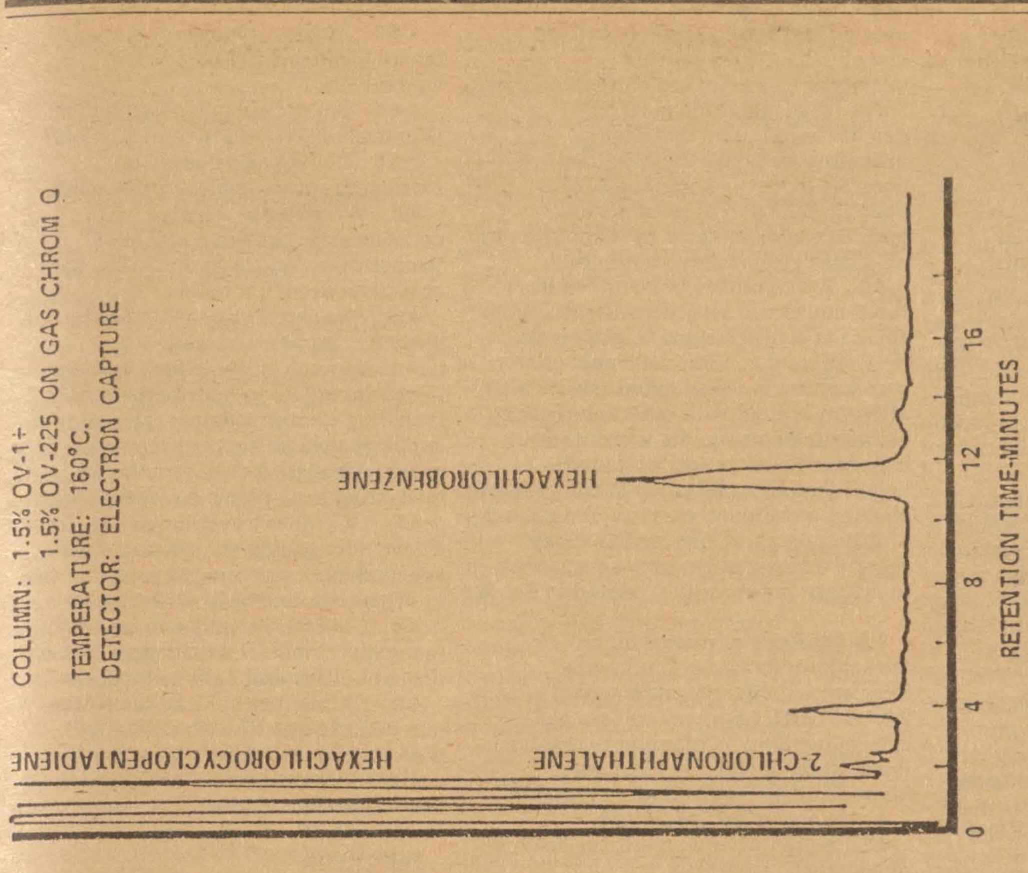

Figure 2. Gas chromatogram of chlorinated hydrocarbons

Appendix II—Gas Chromatographic/Mass Spectrometric Methods: Methods 613, 624 and 625

2,3,7,8,-Tetrachlorodibenzo-p-Dioxin—Method 613

1. *Scope and Application.*

1.1 This method covers the determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). The following parameter may be determined by this method:

Parameter:	*STORET No.*
TCDD	34675

1.2 This method is applicable to the determination of TCDD in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes the potential for finding trace levels of TCDD in the sample. The method incorporates techniques that can also be used to screen samples for TCDD using an electron capture detector.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limit of detection listed in Table I represents the sensitivity that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of this compound, the analyst must take elaborate precautions to prevent exposure to himself, or to others, of materials known or believed to contain TCDD. The appendix to this method contains guidelines and protocols that should serve as minimum safe-handling standards for the laboratory.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and exchanged to hexane while being concentrated to a volume of 1.0 ml or lower. Capillary column GC/MS conditions and internal standard techniques are described which allow for the measurement of TCDD in the extract. Electron capture gas chromatographic conditions are also provided to permit the analyst to use this equipment to prescreen samples before GC/MS analysis.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. TCDD is often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than that of TCDD. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivity stated in Table I.

3.3 The other isomers of tetrachlorodibenzo-p-dioxin may interfere with the measurement of 2,3,7,8-TCDD. Capillary column gas chromatography is required to resolve those isomers that yield virtually identical mass fragmentation patterns.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnels—2000 ml and 500 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus.

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569001–0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture, packed and capillary column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 GC/Mass Spectrometer system—electron ionization source, capable of selected ion monitoring in groups of two or more ions, and related data system.

4.8 Chromatography column—300 mm longx10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

4.9 Chromatography column—400 mm longx11 mm ID with coarse fritted disc at bottom and Teflon stopcock.

4.10 Pipets—Disposable, Pasteur, 150 mm longx5 mm ID (Fisher Scientific Co., No. 13–678–6A or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 10 N and 1 N in distilled water. Wash the solutions with methylene chloride and with hexane.

5.2 Sulfuric acid—(ACS) (1+1) and 1N. For (1+1), mix equal volumes of conc. H_2SO_4 with distilled water. Wash the solutions with methylene chloride and with hexane.

5.3 Methylene chloride, hexane, benzene, tetradecane—Pesticide quality or equivalent.

5.4 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400° C for 4 hrs. in a shallow tray).

5.5 Stock standards—In a glovebox, prepare stock standard solutions of TCDD and ^{37}C1–TCDD (molecular weight 328). The stock solutions are stored in the glovebox, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.6 Silica gel—high purity grade, 100/120 mesh, (Fisher Scientific Co., No. S–679 or equivalent).

5.7 Alumina—neutral, 80/200 mesh (Fisher Scientific Co., No. A–540 or equivalent). Before use activate for 24 hours at 130° C in a foil-covered glass container.

5.8 Activated Coconut Charcoal—50/200 mesh (Fisher Scientific Co., No. 5–690A or equivalent).

6. *Calibration*

6.1 Prepare GC/MS calibration standards for the internal standard technique that will allow for measurement of relative response factors of at least three TCDD/^{37}Cl TCDD ratios. The ^{37}Cl–TCDD concentration in the standards should be fixed and selected to yield a reproducible response at the most sensitive setting of the mass spectrometer.

6.2 Assemble the necessary GC or GC/MS apparatus and establish operating parameters equivalent to those indicated in Table I. Calibrate the GC/MS system according to Eichelberger, et al. (1975). By injecting calibration standards, establish the response factors for TCDD vs. ^{37}Cl–TCDD.

6.3 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.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis, although surrogate spikes are recommended because of the toxicity of TCDD. Where doubt exists over the identification of a peak on the electron capture chromatogram, mass spectroscopy must be used for clarification or confirmation.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

Caution: If there is a remote possibility that the sample contains TCDD at measurable levels, 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 Appendix.

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techiques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 500-ml separatory funnel.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the 500-ml separatory funnel.

9.4 Perform a third extraction in the same mammer. To the combined extracts in the separatory funnel add 100 ml 1 N NaOH. Shake the funnel for 30–60 seconds. Allow the layers to separate and draw the organic layer into a 250 ml Erlenmeyer flask. Discard the aqueous layer and return the organic layer to the separatory funnel. Perform a second wash of the organic layer with 1 N NaOH and discard the aqueous layer.

9.5 In the same manner wash the organic layer twice with 100 ml 1 N H_2SO_4, discarding the aqueous layers.

9.6 Wash the organic layer three times with 100 ml H_2O, discarding the aqueous layers.

9.7 Pour the organic layer extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30-ml methylene chloride to complete the quantitative transfer.

9.8 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. 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 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.9 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the Snyder column. Increase the temperature of the water bath to 80° C. Prewet the Snyder column by adding about 1 ml hexane to the top. Evaporate the solvent as in 9.8. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2-ml of hexane. A 5-ml syringe is recommended for this operation.

9.10 Add a clean boiling chip and attach a micro-Snyder column. Prewet the column by adding about 1 ml hexane to the top. Place the K–D apparatus on the 80° 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 5–10 minutes. 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 for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml hexane. Adjust the extract volume to 1.0 ml with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.11 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.

9.12 The analyst has several options available to him depending upon the nature of the sample and the availability of resources:

9.12.1 If the appearance of the extract or previous experience with the matrix indicates cleanup will be required the analyst should proceed with one or more techniques as described in paragraph 10.

9.12.2 If the analyst wishes to screen the sample for the possible presence of TCDD before GC/MS analysis, he can analyze the extract by packed column or capillary column electron capture detection, as in paragraph 11.

9.12.3 The analyst may proceed directly to GC/MS analysis, paragraph 12.

10. *Cleanup and Separation.*

10.1 Several cleanup column choices are offered to the analyst in this section. Although any of them may be used independently, the silica gel column (10.2) followed immediately by the alumina column (10.3) has been used frequently to overcome background problems encountered by the GC/MS.

10.2 Silica Gel Column Cleanup for TCDD.

10.2.1 Fill a 400 mm long x 11 mm ID chromatography column with silica gel to the 300 mm level, tapping the column gently to settle the silica gel. Add 10 mm anhydrous sodium sulfate to the top of the silica gel.

10.2.2 Preelute the column with 50 ml 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, transfer the entire 1.0 ml sample extract onto the column, using two 2 ml portions of 20% benzene/80% hexane to complete the transfer.

10.2.3 Just prior to exposure of the sodium sulfate layer to the air, add 40 ml 20% benzene/80% hexane to the column. Collect the eluate in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

10.2.4 Evaporate the fraction to 1.0 ml by standard K–D techniques (9.8–9.10). Analyze by ECGC (11), GC/MS (12) or continue cleanup as described below (10.3).

10.3 Alumina Column Cleanup for TCDD.

10.3.1 If the extract is not in hexane, add 0.1–0.2 ml tetradecane keeper and concentrate it at room temperature down to this volume using a stream of dry nitrogen gas. Dilute to 1.0 ml with hexane.

10.3.2 Fill a 300 mm long x 10 mm ID chromatography column with activated alumina to the 150 mm level, tapping the column gently to settle the alumina. Add 10 mm anhydrous sodium sulfate to the top of the alumina.

10.3.3 Preelute the column with 50 ml 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, transfer the entire 1 ml sample extract onto the column, using two additional 2 ml portions of hexane to complete the transfer.

10.3.4 Just prior to exposure of the sodium sulfate layer to the air, add 50 ml 3% methylene chloride/97% hexane (V/V) and continue the elution of the column. Discard the eluate.

10.3.5 Next elute the column with 50 ml 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 by standard K–D technique (9.8–9.10). Analyze by ECGC (11), GC/MS (12) or continue cleanup as described below (10.4).

10.4 Charcoal and Silica-gel Column Cleanup for TCDD.

10.4.1 Prepare a homogeneous mixture of 1 part activated charcoal to 140 parts silica-gel. Fill a 5 mm ID disposable pipet to a length of 50 mm, tapping the column to settle the mixture.

10.4.2 Preelute the column with 5 ml hexane. Discard the eluate and just prior to exposure of the top of the column to the air, transfer an 0.5 ml aliquot of sample extract onto the column, using an additional 0.5 ml hexane to complete the transfer.

10.4.3 Just prior to exposure of the top of the column to the air, add 10 ml hexane and continue the elution of the column. Discard the eluate.

10.4.4 Next, elute the column with 10 ml benzene into a 10 ml K–D concentrator tube. Concentrate the eluate to 1.0 ml with micro-K–D concentration (9.10) on a boiling water bath. Analyze by ECGC (11) or GC/MS (12).

11. *Electron Capture Screening.*

11.1 The sample extracts can be screened by electron capture gas chormatography at the option of the analyst in an effort to reduce the workload on the GC/MS system. Either packed or capillary column techniques may be used for this purpose. The only acceptable conclusions that can be reached with this technique are: (a) TCDD is not detectable at the detection limit of the procedure: (b) TCDD is not present above a stated concentration or control level: and (c) the presence or absence of TCDD is unresolved.

11.2 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the chromatography achieved by the packed column is shown in Figure 1 and by the capillary column in Figure 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.3 For packed column GC, inject 2–5 μl of the sample extract using the solvent-flush technique. A splitless injector is recommended for the capillary system, but for optimum peak geometry a solvent exhange to tetradecane is required (10.3.1). Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.4 If there is no measureable baseline deflection at the retention time of TCDD, report the result as less than the detection limit of the electron capture system.

11.5 If a measurable peak appears within the tolerances of the TCDD retention time of the system, the analyst should proceed to GC/MS (12).

11.6 If the complexity of the chromatogram defies interpretation, the analyst may want to pursue cleanup (10) followed by reanalysis by ECGC, or proceed directly to GC/MS.

12. *GC/MS Analysis.*

12.1 Table I summarizes the recommended capillary column gas chromatographic materials and operating conditions for the instrument. Included in this table is the estimated retention time and sensitivity that should be achieved by this method. An example of the chromatography achieved by this column is shown in Figure 2. Calibrate the system daily, with a minimum at three injections of standard mixtures.

12.2 Add a known amount of ^{37}Cl–TCDD to the sample extract.

12.3 Analyze samples with selected ion monitoring of at least two ions characteristic of TCDD (m/e 320 and m/e 322) and of ^{37}Cl–TCDD (m/e 328). Proof of the presence of TCDD exists if the following conditions are met:

12.3.1 The retention time of the peak in the sample must match that in the standard, within the performance specifications of the analytical system.

12.3.2 The ratio of ions (320:322) must agree within 10% must agree within 10% of that in the standard.

12.3.3 The retention time of the peak maximum for the m/e 320 peak must *exactly* match that of the 322 peak.

12.4 Quantities the TCDD peak from the response relative to the ^{37}Cl–TCDD internal standard.

12.5 If a response is obtained for both ions but is outside the expected ratio, then a co-eluting impurity may be suspected. In this case, another set of ions characteristic of the TCDD molecule, should be analyzed. A good choice of ions is m/e 257 and m/e 259. These ions are useful in characterizing the molecular structure of TCDD. Suspected impurities such as DDE, DDD or PCB residues can be confirmed by checking for their major fragments. These materials can be removed by the cleanup columns. If available, an analysis of the EC chromatogram will provide insight into the complexity of the problem and will determine the manner in which the mass spectrometer will be used.

12.6 If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst should employ cleanup procedures (10) and reanalyze by GC/MS.

12.7 In those circumstances where these procedures do not yield a definitive conclusion, then the use of high resolution mass spectrometry is suggested.

13. *Calculations.*

13.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concantration, ug/l} = \frac{(A)\ (V_t)}{(V)_i\ (V_s)}$$

Where:

A=Nanograms TCDD injected into the GC/MS from the calibration curve.
V_i=Volume of extract injected (μl)
V_t=Volume of total extract (μl)
V_s=Volume of water extracted (ml)

13.2 Report results in micrograms per liter without correction for recovery data When duplicate and spiked samples are analyzed, all data obtained should be reported.

14. *Accuracy and Precision.* No data available at this time.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 6-Dioxin." Report for EPA Contract 68-03-2635 (In preparation).

2. "Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography—Mass Spectrometry Systems," J. W. Eichelberger, L. E. Harris, and W. L. Budde, *Anal. Chem.* 47, 995–1000 (1975).

Table I.—*Gas Chromatography of TCDD*

Column	Retention time (min.)	Detection limit (μg/L)[1]
Packed[2]	7.3	0.003
Glass Capillary[3]	9.5	0.003

[1] Detection limit is calculated from the minimum detactable GC response being equal to five times the GC background noise, assuming a 1 ml effective final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters. Detection levels apply to both electron capture and GC/MS detection.

[2] Packed column conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long x 2 mm ID glass column with 5% methane/95% Argon carrier gas at 25 ml/min flow rate. Column temperature is 220°C.

[3] Glass capillary column conditions: SP-2250 coated on a 30 m long x 0.25 mm ID glass column (Supelco No. 2-3714 or equivalent) with helium carrier gas at 30 cm/sec linear velocity run splitless. Column temperature is 210°C.

Appendix A—Safe Handling Practices for TCDD

Dow Chemical U.S.A. has issued the following precautions for safe handling TCDD in the laboratory. In addition to these practices, the following points are also helpful:

1. Contamination of the laboratory will be minimized by conducting all manipulations in the hood.

2. Effluent of the gas chromatography (from the Nickel-63 detector or as a result of splitting when capillary columns are used) should pass through either a column of activated charcoal or bubbled through a trap containing oil or high-boiling alcohols.

3. Liquid waste can be dissolved in methanol or ethanol and irradiated with ultraviolet light with wavelength greater than 290 nm for several days.

Precautions for Safe Handling of 2,3,7,8-Tetrachlorodibenzo-Para-Dioxin (TCDD) in the Laboratory (Revised 11/78)

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.

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 TCDD.

Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.

Training: Workers must be trained in the proper method of getting out of contaminated gloves and clothing without contacting the exterior surfaces.

Personel Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in safe handling of waste (one accidental case of chloracne resulted from handling laboratory waste in a routine manner).

Disposal of Wastes: TCDD decomposes above 800°C. Low-level waste such as the 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.

Decontamination: Personal—any mild soap with plenty of scrubbing action: *Glassware, Tools, and Surfaces*—Chlorothene[1] NU Solvent 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. Dish water 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.

Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Wastes." Lab coats or other clothing worn in TCDD work 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

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[1] Trademark of the Dow Chemical Company.

the problem. The washer should be run through a cycle before being used again for other clothing.

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 microgram per wipe. The analytical method is available upon request. Less than 1 microgram TCDD per sample indicates acceptable clealiness; anything higher warrants further cleaning. More than 10 micrograms on a wipe sample indicates an acute hazard and requires prompt cleaning before further use of the equipment or work space. It indicates further that unacceptably sloppy work habits have been employed in the past.

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 case of an accident.

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.

For clinical advice, contact B. B. Holder, M.D., Medical Director, Dow Chemical U.S.A., Midland, Michigan 48640, (telephone 517/636-2108). For detailed safe handling precautions for specific procedures, contact L. G. Silverstein, Industrial Hygiene Laboratory, Dow Chemical U.S.A., Midland, Michigan 48640 (telephone 517/636-1688).

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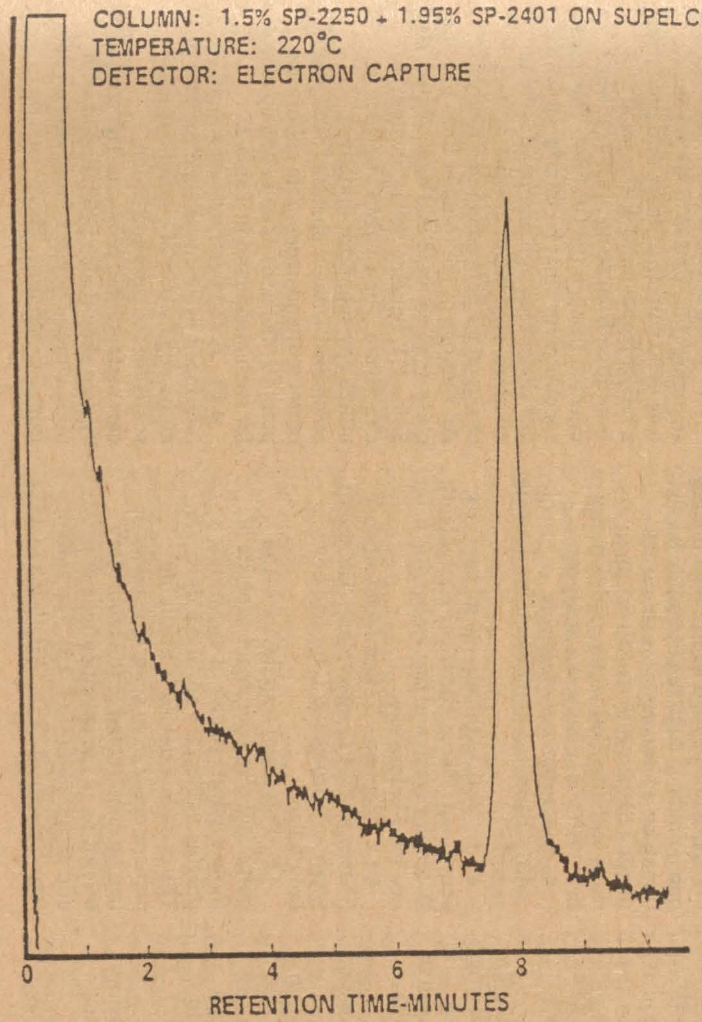

Figure 1. Gas chromatogram of TCDD

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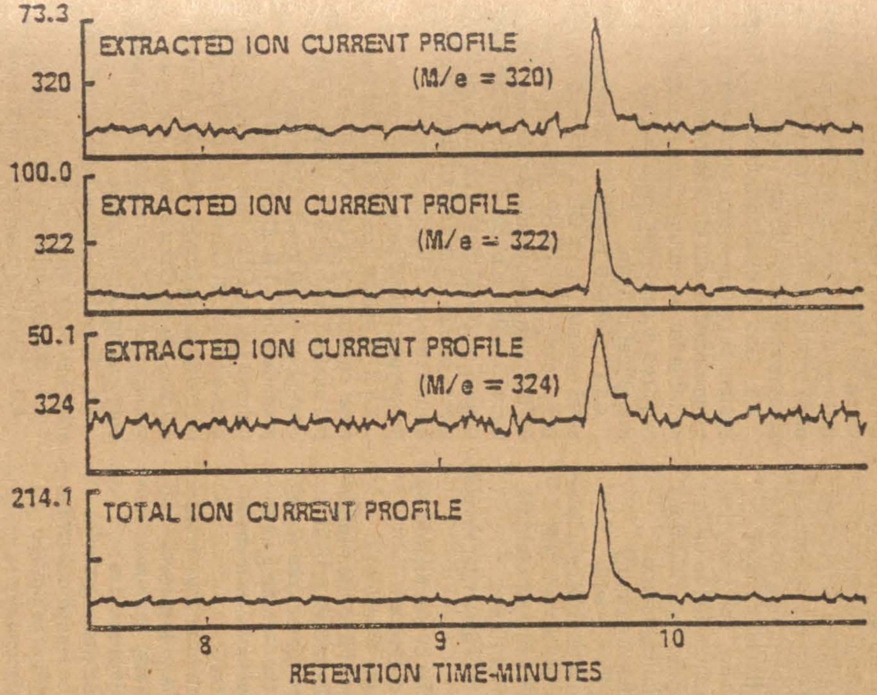

Figure 2. Total and extracted ion current profiles of TCDD

Purgeables—Method 624

1. *Scope and Application.*

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

21. A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free 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 soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1. Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ⅛ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60–80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten centimeter traps may be used providing that the recoveries are comparable to the 25 cm traps.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD x 0.90 to 0.105 in. ID) packed with 1% SP–1000 coated on 60/80 mesh Carbopack B preceded by a 5-cm precolumn packed with 1% SP–1000 coated on 60/80 mesh Chromosorb W. A glass column (¼ in OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in OD x 0.09 to 0.105 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (¼ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–260 in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.3 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—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 worn when the analyst handles high concentrations of such materials.

5.5.1 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 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 μl syringe, immediately add 2 to 3 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.

5.5.2.2 Gases—To prepare standards of 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 methyl alcohol menicus. Slowly inject the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle equipped with a Teflon cap liner.

5.5.4 Calculate the concentration in mg per ml (equivalent to μg per μl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 μg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. *Calibration.*

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 μg/l, for example, prepare secondary methanolic standards at 100 μg/l, and 500 μg/l, so that aqueous standards prepared from thee secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the limit of detection requirements in Table 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample analysis may begin.

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in μg.

C_s is the amount of the pollutant standard in μg.

The relative response ratio for each pollutant should be known for at least two concentration values—50 ng injected to approximate 10 μg/l and 500 ng to approximate the 100 μg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. The response factor (RF) must be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note.—EPA, through its contractors and certain of its Regional Laboratories, is currently evaluating selected compounds for use as internal standards in the analysis of organics by purge and trap.

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 μg/40 ml) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 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 until it overflows. 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 5.0 μl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ±.05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap, with an inert gas, at 20 to 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 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 organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device 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 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. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. *Gas Chromatography—Mass Spectrometry.*

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operting conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 5.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS–1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

Sample size—5.0 ml.
Purge gas—Helium, high purity grade.
Purge time—12 minutes.
Purge flow—40 ml/min.
Trap dimensions—⅛ in. O.D. (0.105 in. I.D.)x25 cm long.
Trap sorbent—Tenax-GC, 60/80 mesh (15 cm), plus Type 15 silica gel, 35/60 mesh (8 cm).
Desorption flow—20 ml/min.
Desorption time—4 min.
Desorption temperature—180° C.

10.4 Mass Spectrometer Parameters.

Electron energy—70 volts (nominal).
Mass range—20–27, 33–260 amu.
Scan time—6 seconds or less.

10.5 Calibration of the gas chromatography-mass spectrometry (GC-MS system—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP or BFB.

10.5.1 To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP-2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 3 are met.

10.5.2 To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 4 are met.

10.5.3 If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

10.6 Analyze an internal or external calibration standard to develop response factors for each compound.

11. *Qualitative and Quantitative Determination.*

11.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table 5. The criteria below must be met for a qualitative identification.

11.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

11.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

11.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC-MS system or from a reference library.

11.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.2 The primary ion listed in Table 5 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

11.3 For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses listed for the compounds in Table 5 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

11.4 Internal Standard Method Calculations—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of the pollutant (C_o) in μg/l in the sample is calculated using equation 2,

$$\text{Eq. (2)} C_o = \frac{(A_s)(C_{is})}{(A_{is})(RF)(V_o)}$$

Where:

V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.5. To quantify, add the internal standard to the 5.0 ml sample no more than a few minutes before purging to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve.

11.5 Extenral Standard Method Calculations—The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. (3) micrograms per liter} = \text{ng/ml} = \frac{(A)}{(V_s)}$$

Where:

A = Mass of compound from calibration curve (ng/5 ml).
V_s = volume of water purged (5 ml).

11.6 An alternate external standard approach for purgeables utilizes a single point calibration. Prepare and analyze a reference standard that closely approximates the response for each component in a sample. Calculate the concentration in the sample using Equation 4.

$$\text{Eq. 4 micrograms per liter} = \frac{(A)(B)}{(C)}$$

Where:

A = area of the unknown
B = concentration of standard (μg/l)
C = area of the standard.

11.7 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported. Report results in micrograms per liter without correction for recovery data.

12. *References.*

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2. "Symposium on Measurement of Organic Pollutants in Water and Wastewater," ASTM Special Publication, 1979 (In Press).

3. "Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," T. A. Bellar and J. J. Lichtenberg, *Jour. AWWA, 66*, 739–744, Dec. 1974.

4. ASTM Annual Standards—Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

5. ASTM Annual Standards—Water, part 31, Method D3371 "Tentative Method of Test for Nitriles in Aqueous Solution of Gas Liquid Chromatograph."

6. "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry," Harris, L. E., Budde, W. L., and Eichelberger, J. W. *Anal. Chem., 46*, 1912 (1974).

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1. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," March 1977 (revised April 1977). USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

2. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1—Denver, Colorado, November 1977; Volume 2—Savannah, Georgia, May 1978; Volume 3—Norfolk, Virginia, March 1979; USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1

Parameter	STORET No.
Acrolein	34210
Acrylonitrile	34215
Benzene	34236
Bromomethane	34413
Bromodichloromethane	32101
Bromoform	32104
Carbon Tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34105
1,1-Dichloroethane	34496

Table 1—Continued

Parameter	STORET No.
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Ethylbenzene	34371
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachlorethene	34475
1,1,1-Trichloroethane	34506
1,1,2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34488
Toluene	34010
Vinyl chloride	39175

Table 2.—*Gas Chromatography of Organics by Purge and Trap*

Compound	Retention time (minutes)		Limit of detection[3] (µg/l)
	Col. 1[1]	Col. 2[2]	
chloromethane	1.50	2.10	10
bromomethane	2.17	2.50	10
vinyl chloride	2.67	2.57	10
chloroethane	3.33	2.82	10
methylene chloride	5.25	4.03	10
trichlorofluoromethane	7.18	5.14	10
1,1-dichloroethene	7.92	5.25	10
bromochloromethane (SS)	8.48	6.31	
1,1-dichloroethane	9.30	6.48	10
trans-1,2-dichloroethene	10.08	6.81	10
chloroform	10.68	7.70	10
1,2-dichloroethane	11.40	8.29	10
1,1,1-trichloroethane	12.60	9.28	10
carbon tetrachloride	13.02	9.45	10
bromodichloromethane	13.65	10.36	10
1,2-dichloropropane	14.92	11.30	10
trans-1,3-dichloropropene	15.22	11.70	10
trichloroethene	15.80	11.98	10
dibromochloromethane	16.48	12.86	10
1,1,2-trichloroethane	16.52	12.86	10
cis-1,3-dichloropropene	16.53	12.86	10
benzene		12.95	10
2-chloroethylvinyl ether	18.00	13.71	10
2-bromo-1-chloropropane (SS)		13.82	
bromoform	19.23	15.41	10
1,1,2,2-tetrachloroethane	21.62	17.70	10
tetrachloroethene	21.67	17.44	10
1,4-dichlorobutane (SS)		18.13	
toluene		18.53	10
chlorobenzene	24.18	20.57	10
ethylbenzene		25.06	10
acrolein			[4]100
acrylonitrile			[4]100

[1] Eight ft. stainless steel column (1/8 in ODx0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 1 ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. (A glass column (1/4 in. ODx2 mm ID) may be substituted). Carrier gas helium at 40 ml/min. Temperature program: 3 min isothermal at 45° C, then 8°/min to 220°, hold at 220° for 15 minutes.

[2] Eight ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (1/4 in. ODx2 mm ID) may be substituted. Carrier gas: helium at 40 ml/min. Temperature program: 3 min. isothermal at 60° C then 8°/min to 160°, hold at 160 until all compounds elute.

[3] This is a minimum level at which the entire system must give recognizable mass spectra and acceptable calibration points.

[4] Sensitivity refers to either this method or direct aqueous injection GC-FID (Ref. 4,5,6).

Table 3.—*DFTPP Key Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
51	30 to 60 pct of mass 198.
68	Less than 2 pct of mass 69.
70	Less than 2 pct of mass 69.
127	40 to 60 pct of mass 198.
197	Less than 1 pct of mass 198.
198	Base peak, 100 pct relative abundance.
199	5 to 9 pct of mass 198.
275	10 to 30 pct of mass 198.
365	Greater than 1 pct of mass 198.
441	Present but less than mass 443.
442	Greater than 40 pct of mass 198.
443	17 to 23 pct of mass 442.

Table 4.—*BFB Keyt Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
50	20 to 40 pct of mass 95.
75	50 to 70 pct of mass 95.
95	Base peak, 100 pct relative abundance.
96	5 to 9 pct of mass 95.
173	Less than 1 pct of mass 95.
174	70 to 90 pct of mass 95.
175	5 to 9 pct of mass 95.
176	70 to 90 pct of mass 95.
177	5 to 9 pct of mass 95.

Table 5.—*Characteristic Ions of Volatile Organics*

Compound	E I ions				Primary ion
chloromethane	50	52			50
bromomethane	94	96			94
vinyl chloride	62	64			62
chloroethane	64	66			64
methylene chloride	49	51	84	86	84
trichlorofluoromethane	101	103			101
1,1-dichloroethene	61	96	98		96
bromochloromethane (SS)	49	130	128	51	128
1,1-dichloroethane	63	65	83		63
	85	98	100		
trans-1,2-dichloroethene	61	96	98		96
chloroform	83	85			83
1,2-dichloroethane	62	64	98	100	98
1,1,1-trichloroethane	97	99	117	119	97
carbon tetrachloride	117	119	121		117
bromodichloromethane	83	85	127	129	127
1,2-dichloropropane	63	65	112	114	112
trans-1,3-dichloropropene	75	77			75
trichloroethene	95	97	130	132	130
dibromochloromethane	129	127	208	206	127
cis-1,3-dichloropropene	75	77			75
1,1,2-trichloroethane	83	85	97		
	99	132	134		97
benzene	78				78
2-chloroethytlvinyl ether	63	65	106		106
2-bromo-1-chloropropane (SS)	77	79	156		77
bromoform	171	173	175	250	173
	252	254	256		
tetrachloroethenbe	129	131	164	166	164
1,1,2,2-tetrachloroethane	83	85	131	133	
	166	168			168
1,4-dichlorobutane (SS)	55	90	92		55
toluene	91	92			92
chlorobenzene	112	114			112
ethylbenzene	91	106			106
acrolein	26	27	55	56	56
acrylonitrile	26	51	52	53	53

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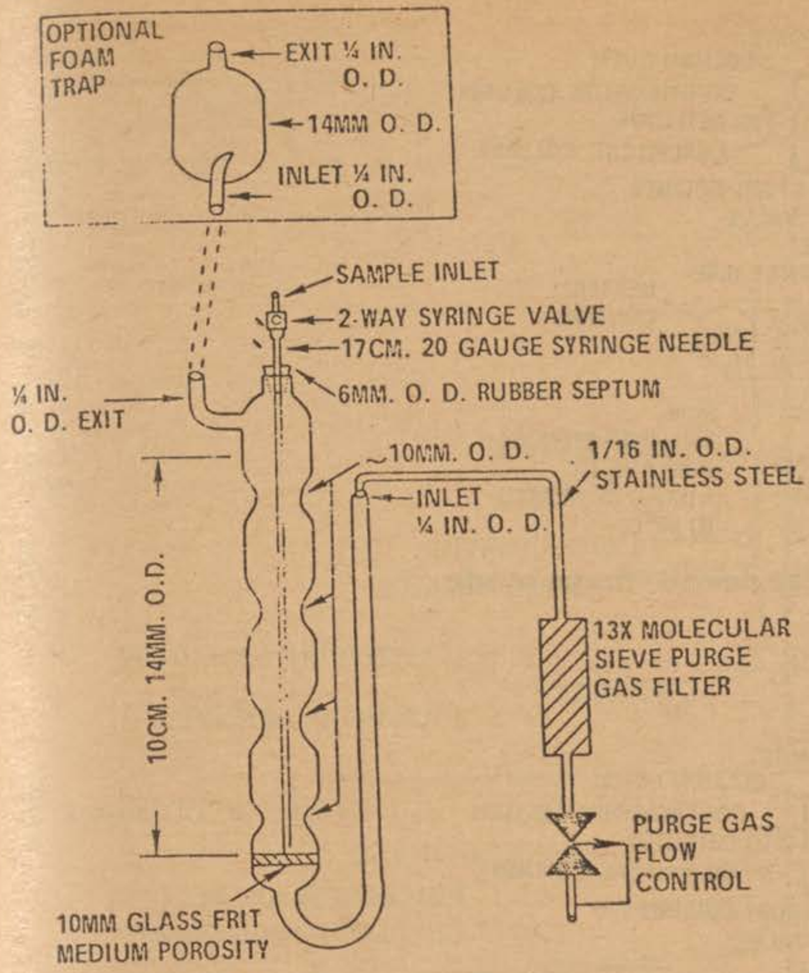

Figure 1. Purging device

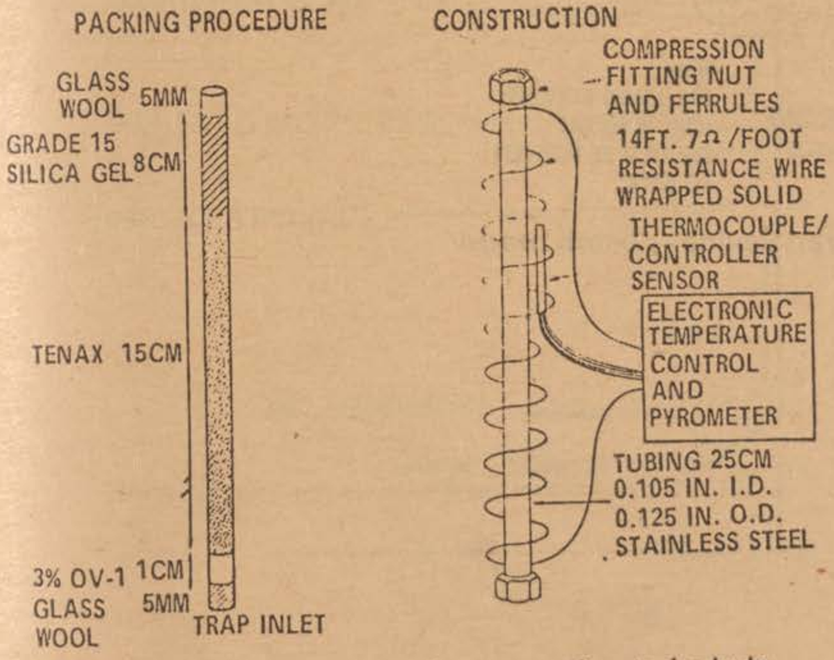

Figure 2. Trap packings and construction to include desorb capability

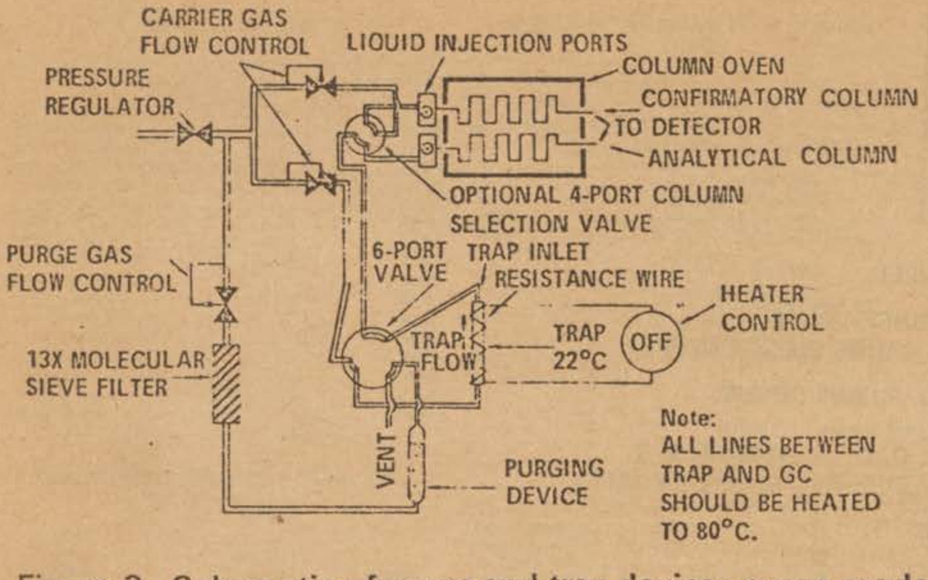

Figure 3. Schematic of purge and trap device - purge mode

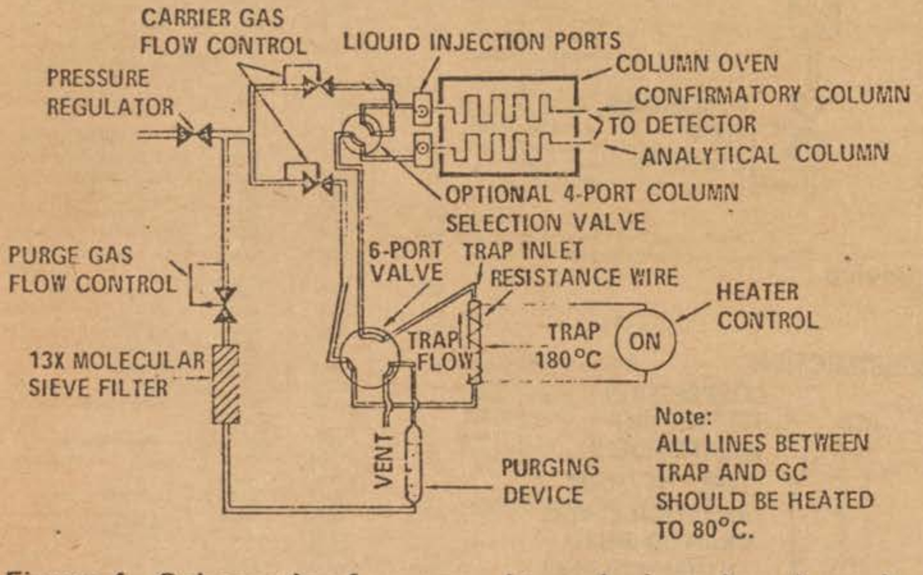

Figure 4. Schematic of purge and trap device - desorb mode

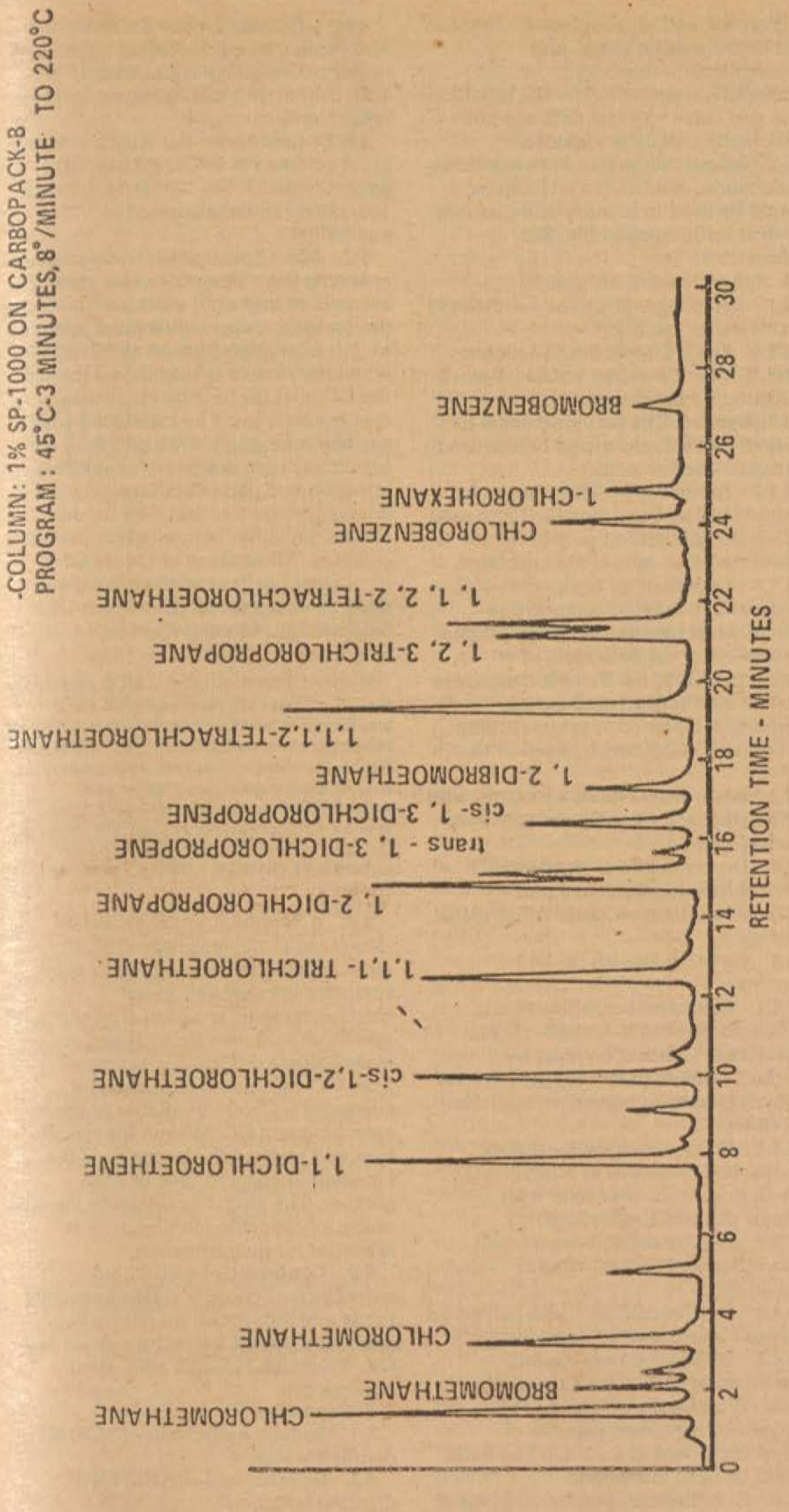

Figure 5. Gas chromatogram of volatile organics by purge and trap

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Base/Neutrals, Acids, and Pesticides—Method 625

1. *Scope and Application.*

1.1 This method covers the determination of a number of organic compounds that are solvent extractable and amenable to gas chromatography. The parameters listed in Tables 1, 2 and 3 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 4, 5, and 6 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.

1.4 The GC/MS parts of this method are recommended for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1 to 2 liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ml using a Kuderna-Danish (K–D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.

2.2 Quantitative analysis is performed by GC/MS using either the internal standard or external standard technique.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. Alternative techniques should be used to identify and quantify these specific compounds. See Reference 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter to 1-gallon volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to fit sample bottles. Caps must be lined with Teflon. Aluminum foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 1000 ml. Sample containers must be kept refrigerated during sampling. No plastic or rubber tubing other than Teflon may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock (Ace Glass 7228–T–72 or equivalent).

4.3 Drying column—A 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0232 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569002–0219 or equivalent).

4.4.5 Boiling chips-extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.

4.6.1 Column 1—For Base/Neutral and Pesticides a 6-foot glass column (¼ in OD x 2 mm ID) packed with 3% SP–2250 coated on 100/120 Supelcoport (or equivalent).

4.6.2 Column 2—For Acids, a 6-foot glass column (¼ in OD x 2 mm ID) packed with 1% SP–1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

4.7 Mass Spectrometer—Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (Reference 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note.—Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives recognizable mass spectra and acceptable calibration points at the limit of detection specified for each individual compound listed in Tables 4, 5, and 6.

4.8 A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be computer software available to allow searching any GC–MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

4.9 Continuous liquid-liquid extractors—Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor—Ace Glass Co., Vineland, N.J. P/N 6841–10 or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 6N in distilled water.

5.2 Sulfuric acid—(ACS) 6N in distilled water.

5.3 Sodium sulfate—(ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400° C for 4 hrs.).

5.4 Methylene chloride—Pesticide quality or equivalent.

5.5 Stock standards—Obtain stock standard solutions at a concentration of 1.00 μg/μl. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them. Protect PNA standards from light.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will bracket the working range of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables 4, 5, or 6) can be calculated as 20 ng injected, for example, prepare standards at 1 μg/ml, 10 μg/ml, 100 μg/ml, etc. so that injections of 1–5 μl of the calibration standards will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Tables 4, 5, and 6. By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the limits of detection requirements of Tables 4, 5, and 6. If the sample gives peak areas above the working range, dilute and reanalyze.

6.3 Internal Standard Method—The internal standard approach is acceptable for all of the semivolatile organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. 1 $RF=(A_sC_{is})/(A_{is}C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount (μg) of the internal standard.

C_s is the amount (μg) of the pollutant standard.

6.3 The relative response ratio for the pollutants should be known for at least two concentration values—20 ng injected to approximate 10 μg/l and 200 ng injected to approximate the 100 μg/l level. (Assuming 1 ml final volume and a 2 μl injection). Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response.

The response factor (RF) should be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same (20 μg) so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s), using a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed. To quantify, add the internal standard to the concentrated sample extract no more than a few minutes before injecting into the GC/MS to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve. Either deuterated or fluorinated compounds can be used as internal standards and surrogate standards. Naphthalene-d_8, anthracene-d_{10}, pyridine-d_5, aniline-d_5, nitrobenzene-d_5, 1-fluoronaphthalene, 2-fluoronaphthalene, 2-fluorobiphenyl, 2,2′-difluorobiphenyl, and 1,2,3,4,5-pentafluorobiphenyl have been used or suggested as appropriate internal standards/surrogates for the base-neutral compounds. Phenol-d_6, pentafluorophenol, 2-perfluoromethyl phenol, and 2-fluorophenol have been used or suggested for the acid compounds. Compounds used as internal standards are not to be used as surrogate standards. The internal standard must be different from the surrogate standards.

6.5 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the limit of detection (Tables 4, 5, and 6). After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, demonstrate through the analysis of a method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

8. *Sample Collection, Preservation, and Handling.*

8.1 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 free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction (Base/Neutrals, Acids, and Pesticides).*

9.1 Samples may be extracted by separatory funnel techniques or with a continuous extractor as described in Section 10. Where emulsions prevent acceptable solvent recovery with the separatory funnel technique, the analyst must use the continuous extractor.

9.2 The details of the extraction technique should be adjusted according to the sample volume. The technique described below assumes a sample volume of 1000 ml. For volumes approximating 2-liters, the volume of extraction solvent should be adjusted to 250, 100, and 100 ml for the serial extraction of the base neutrals, and 200, 100, and 100 ml for the acids.

9.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the pH of the sample with 6N NaOH to 11 or greater. Use multirange pH paper for the measurements. Proceed to Section 10 if continuous extraction is used.

9.4 Add 60 ml methylene chloride to the sample bottle, cap, and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size 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, or centrifugation. (If the emulsion cannot be broken, that is, recovery is less than 80% of the added solvent corrected for the water solubility of methylene chloride, transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10). Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.5 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with 10 ml concentrator tube. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride. Pour this through the drying column. Seal, label as base/neutral fraction, and proceed with the acid extraction. If the extract must be stored overnight before analysis by GC/MS, it may be transferred to a 2 ml serum vial equipped with a Teflon-lined rubber septum and crimp cap.

9.7 Acid (Phenols) Extraction—Adjust the pH of the water, previously extracted for base-neutrals, with 6N H_2SO_4 to 2 or below. Serially extract with 60, 60 and 60 ml portions of distilled-in-glass methylene chloride. Collect and combine the extracts in a 250-ml Erlenmeyer flask then dry by passing through a column of anhydrous sodium sulfate. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride and pour through the drying column. Seal, label acid fraction and prepare for concentration.

9.8 Concentrate the extracts (Base/Neutrals and Acids) in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

9.9 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. 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 actively chatter but the chambers do not flood. When the liquid has reached an apparent volume 1 ml, remove the K–D apparatus and allow the solvent to drain for at least 10 minutes while cooling. 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.

9.10 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube in 9.8. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus 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 actively chatter but the chambers do not flood. When the liquid reaches an apparent volume of about 0.5 ml, remove the K–D from the water bath and allow the solvent to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the final volume to 1.0 ml, seal, and label as acid fraction.

9.11 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.

10. *Emulsions/Continuous Extraction.*

10.1 Place 100 to 150 ml of methylene chloride in the extractor and 200–500 ml methylene chloride in the distilling flask.

10.2 Add the aqueous sample (pH 11 or greater) to the extractor. Add blank water as necessary to operate the extractor and extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride in a 500 ml K–D evaporator flask quipped with a 10 ml concentrator tube. Seal, label as the base/neutral fraction, and concentrate as per sections 9.8 to 9.10.

10.3 Adjust the pH of the sample in the continuous extractor to 2 or below using 6N sulfuric acid. Charge a clean distilling flask with 500 ml of methylene chloride. Extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride layer on a K–D evaporator flask equipped with a 10 ml concentrator tube. Label as the acid fraction. Concentrate as per sections 9.8 to 9.10.

11. *Calibration of the GC–MS System.*

11.1 At the beginning of each day, the mass calibration of the GC–MS system must be checked and adjusted if necessary to meet DFTPP specifications (11.3). Each day base-neutrals are measured, the column performance specification (12.1) with benzidine must be met. Each day the acids are measured, the column performance specification (13.1) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

11.2 To perform the mass calibration test of the GC–MS system, the following instrumental parameters are required:

Electron energy—70 volts (nominal).
Mass range—35 to 450 a.m.u.
Scan time—7 seconds or less.

11.3 GC–MS system calibration—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ug DFTPP and check to insure that performance criteria listed in Table 10 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. *Gas Chromatography-Mass Spectrometry of Base/Neutral Fraction.*

12.1 At the beginning of each day that base/neutral analyses are to be performed, inject 100 nanograms of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. The tailing factor for benzidine should be less than 3. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

12.2 Establish chromatographic conditions equivalent to those in Tables 4 and 5. Included in these tables are estimated retention times and sensitivities that can be achieved by this method. Examples of the separatioins achieved by these columns are shown in Figures 1 and 3 through 7.

12.3 Program the GC/MS to operate in the Extracted Ion Current Profile (EICP) mode, and collect EICP for the three ions listed in Tables 7 and 8 for each compound being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6, using either the internal or external standard procedure.

12.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 14° C.

13. *Gas Chromatography/Mass Spectrometry of Acid Fraction.*

13.1 At the beginning of each day that acid fraction analyses are to be performed, inject 50 nanograms of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. The tailing factor for pentachlorophenol should be less than 5. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

13.2 Establish chromatographic conditions equivalent to those in Table 6. Included in this table are estimated retention times and sensitivities that can be achieved by this method. An example of the separation achieved by the column is shown in Figure 2.

13.3 Program the GC/MS to operate in the Extracted Ion Current Profile mode, and collect EICP for the three ions listed in Table 9 for each phenol being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6 using either the internal or external standard procedure.

13.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

13.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external standard calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

13.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

14. *Qualitative and Quantitative Determination.*

14.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and the two other ions listed in Tables 7, 8, or 9. The criteria below must be met for a qualitative identification.

14.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

14.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

14.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

14.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.2 In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables 7 and 8 characteristic CI ions for most of the compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

14.3 When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables 7, 8 and 9. If the sample produces an interference for the first listed ion, use a secondary ion to quantify. Quantification will be done by the external or internal standard method.

14.4 Internal Standard—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of pollutant (C_o) is μg/l in the sample is calculated using equation 2.

$$\text{Eq. 2} \qquad C_o = \frac{(A_s)\ (C_{is})}{(A_{is})\ (RF)\ (Vo)}$$

Where: V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.3.

14.5 External Standard—The concentration of the unknown can be calculated from the slope and intercept of the calibration curve. The unknown concentration can be determined using equation 3.

Eq. 3

$$\text{Micrograms/liter} = \text{ng/ml} = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A=mass of compound from calibration curve (ng).

V_i=volume of extract injected (μl).

V_t=volume of total extract (μl).

V_s=volume of water extracted (ml).

14.6 Report all results to two significant figures. Report results in micrograms per liter (Base/Neutrals and Acids) without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14.7 In order to minimize unnecessary GC–MS analysis of method blanks and field blanks, the field blank may be screened on a FID–GC equipped with the appropriate SP–2250 or SP–1240 DA columns.

15. **References**

1. Method 610, Polynuclear Aromatic Hydrocarbons, EMSL, Cincinnati, Ohio 45268, 1979.
2. "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,* 995–1000 (1975).

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2. "Proceedings.—Seminar on Analytical Methods for Priority Pollutants":

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   USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1.—*Base-Neutral Extractables*

Compound	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(b)fluoranthene	34230
Benzo(k)fluoranthene	34242
Benzo(a)pyrene	34247
Benzo(g,h,i)perylene	34521
Benzidine	39120
Bis(2-chloroethyl)ether	34273
Bis(2-chloroethoxy)methane	34278
Bis(2-ethylhexyl)phthalate	39100
Bis(2-chloroisopropyl)ether	34283
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Di-n-butylphthalate	39110
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
1,2-Dichlorobenzene	34536
3,3'-Dichlorobenzidine	34631
Diethylphthalate	34336
Dimethylphthalate	34341
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Dioctylphthalate	34596
1,2-Diphenylhydrazine	34346
Fluoranthane	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
Hexachlorocyclopentadiene	34386
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	39250
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodi-n-propylamine	34428
N-Nitrosodiphenylamine	34433
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

Table 2.—*Acid Extractables*

Compound	STORET No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39094
Phenol	34694
2,4,6-Trichlorophenol	34621

Table 3.—*Pesticide Extractables*

Compound	STORET No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39340
g-BHC	34259
Chlordane	39350
4,4'-DDD	39310
4,4'DDE	39320
4,4'DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

Table 4—*Gas Chromatography of Base/Neutral Extractables*

Compound	Retention time # (min.)	Limit of detection ##	
		ng injected	μg/1
1,3-Dichlorobenzene	7.4	20	10
1,4-Dichlorobenzene	7.8	20	10
Hexachloroethane	8.4	20	10
Bis(2-chloroethyl)ether	8.4	20	10
1,2-Dichlorobenzene	8.4	20	10
Bis(2-chloroisoprooyl)ether	9.3	20	10
N-nitroso-di-n-propyl amine		20	10
Nitrobenzene	11.1	20	10
Hexachlorobutadiene	11.4	20	10
1,2,4-Trichlorobenzene	11.6	20	10
Isophorone	11.9	20	10
Naphthalene	12.1	20	10
Bis(2-chloroethoxy) methane	12.2	20	10
Hexachlorocyclopentadiene	13.9	20	10
2-Chloronaphthalene	15.9	20	10
Acenaphthylene	17.4	20	10
Acenaphthene	17.8	20	10
Dimethyl phthalate	18.3	20	10
2,6-Dinitrotoluene	18.7	20	10
Fluorene	19.5	20	10
4-Chlorophenyl phenyl ether	19.5	20	10
2,4-Dinitrotoluene	19.8	20	10
1,2-Diphenyl hydrazine*	20.1	20	10
Diethyl phthalate	20.1	20	10
N-nitrosodiphenyl amine**	20.5	20	10
Hexachlorobenzene	21.0	20	10
4-Bromophenyl phenyl ether	21.2	20	10
Phenanthrene	22.8	20	10
Anthracene	22.8	20	10
Di-n-butyl phthalate	24.7	20	10
Fluoranthene	26.5	20	10
Pyrene	27.3	20	10
Benzidine	28.8	20	10
Butyl benzyl phthalate	29.9	20	10
Bis(2-ethylhexyl) phthalate	30.6	20	10
Chrysene	31.5	20	10
Benzo(a)anthracene	31.5	20	10
3,3'-Dichlorobenzidine	32.2	20	10
Di-n-octyl phthalate	32.5	20	10
Benzo(b)fluoranthene	34.9	20	10
Benzo(k)fluoranthene	34.9	20	10
Benzo(a)pyrene	36.4	20	10
Indeno(1,2,3-c,d)pyrene	42.7	50	25
Dibenzo(a,h)anthracene	43.2	50	25
Benzo(g,h,i)perylene	45.1	50	25
N-Nitrosodimethylamine			
Bis(chloromethyl)ether			
2,3,7,8-Tetrachlorodibenzo-p-dioxin			

#Six foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per min to 270° C. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

##This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 μl injection of a one liter sample that has been extracted and concentrated to a volume of 1.0 ml.)

*Detected as azobenzene.

**Detected as diphenylamine.

Table 5.—*Gas Chromatography of Pesticide Extractables*

Compound	Retention time (min)*	Limit of detection#	
		ng injected	μg/l
a-bhc	21.1	40	10
g-bhc	22.4	40	10
b-bhc	23.4	40	10
Heptachlor	23.4	40	10
d-bhc	23.7	40	10
Aldrin	24.0	40	10
Heptachlor epoxide	25.6	40	10
Endosulfan I	26.4	40	10
Dieldrin	27.2	40	10
4,4'-DDE	27.2	40	10
Endrin	27.9	40	10
Endosulfan II	28.6	40	10
4,4'-DDD	28.6	40	10
4,4'-DDT	29.3	40	10
Endosulfan sulfate	29.8	40	10
Chlordane	19 to 30		
Toxaphene	25 to 34		
PCB-1242	20 to 32		
PCB-1254	23 to 32		

*6 foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per minute to 270°. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 4 μl injection of a one-liter sample that has been extracted and concentrated to a volume of 1.0 ml.

Table 6.—*Gas Chromatography of Acid Extractables*

Compound	Retention time* (min)	Limit of detection#	
		ng injected	μg/l
2-Chlorophenol	5.9	50	25
2-Nitrophenol	6.4	50	25
Phenol	8.0	50	25
2,4-Dimethylphenol	9.4	50	25
2,4-Dichlorophenol	9.8	50	25
2,4,6-Trichlorophenol	11.8	50	25
4-Chloro-3-methylphenol	13.2	50	25
2,4-Dinitrophenol	15.9	500	250

Table 6.—*Gas Chromatography of Acid Extractables*—Continued

Compound	Retention time* (min)	Limit of detection#	
		ng injected	μg/l
2-Methyl-4,6-dinitrophenol	16.2	500	250
Pentachlorophenol	17.5	50	25
4-Nitrophenol	20.3	50	25

*6 foot glass column (¼ in. OD x 2 mm ID) Packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: 2 min isothermal at 70°, then 8° per min to 200° C. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 μl injection of a one liter sample that has been extracted and concentrated to 1.0 ml.)

Table 7.—*Base/Neutral Extractables Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
1,3-Dichlorobenzene	146	148	113	146	148	150
1,4-Dichlorobenzene	146	148	113	146	148	150
Hexachloroethane	117	201	199	199	201	203
Bis(2-chloroethyl) ether	93	63	95	63	107	109
1,2-Dichlorobenzene	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	45	77	79	77	135	137
N-Nitrosodipropyl amine	130	42	101			
Isophorone	82	95	138	139	167	178
Nitrobenzene	77	123	65	124	152	164
Hexachlorobutadiene	225	223	227	223	225	227
1,2,4-Trichlorobenzene	180	182	145	181	183	209
Naphthalene	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	93	95	123	65	107	137
Hexachlorocyclopentadiene	237	235	272	235	237	239
2-Chloronaphthalene	162	164	127	163	191	203
Acenaphthylene	152	151	153	152	153	181
Acenaphthene	154	153	152	154	155	183
Dimethyl phthalate	63	194	164	151	163	164
2,6-Dinitrotoluene	165	63	121	83	211	223
Fluorene	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	204	206	141			
2,4-Dinitrotoluene	165	89	163	183	211	223
1,2-Diphenylhydrazine[1]	77	93	105	185	213	225
Diethylphthalate	149	177	150	177	223	251
N-Nitrosodiphenylamine[2]	169	168	167	169	170	198
Hexachlorobenzene	284	142	249	284	286	288
4-Bromophenyl phenyl ether	248	250	141	249	251	277
Phenanthrene	178	179	176	178	179	207
Anthracene	178	179	176	178	179	207
Dibutyl phthalate	149	150	104	149	205	279
Fluoranthene	202	101	100	203	231	243
Pyrene	202	101	100	203	231	243
Benzidine	184	92	185	185	213	225
Butyl benzyl phthalate	149	91		149	299	327
Bis(2-ethyl hexyl) phthalate	149	167	279	149		
Chrysene	228	226	229	228	229	257
Benzo(a)anthracene	228	229	226	228	229	257
3,3'-Dichlorobenzidine	252	254	126			
Dioctyl phthalate	149					
Benzo(b)fluoranthene	252	253	125	252	253	281
Benzo(k)fluoranthene	252	253	125	252	253	281
Benzo(a)pyrene	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	276	138	277	276	277	305
Dibenzo(a,h)anthracene	278	139	279	278	279	307
Benzo(g,h,i)perylene	276	138	277	276	277	305
N-nitrosodimethyl amine	42	74	44			
Bis(chloromethyl) ether	45	49	51			
2,3,7,8-Tetrachlorodibenzo-p-dioxin		322	320	59		
Deuterated anthracene(d–10)[3]	188	94	80	189	217	

[1] Detected as azobenzene.

[2] Detected as diphenylamine.

[3] Suggested internal standard.

Table 8.—*Pesticides Characteristic Ions*

Compound	Characteristic ions electron impact		
a-BHC	183	181	109
g-BHC	183	181	109
b-BHC	181	183	109
heptachlor	100	272	274
d-BHC	183	109	181
aldrin	66	263	220
heptachlor epoxide	353	355	351
endosulfan I	201	283	278
dieldrin	79	263	279
4,4'-DDE	246	248	176
4,4'-DDD	235	165	237
endrin	81	263	82
endosulfan II	201	283	278
4,4'-DDT	235	237	165
endosulfan sulfate	272	387	422
chlordane [1]	373	375	377
toxaphene [2]	231	233	235
PCB-1242 [2]	224	260	294
PCB-1254 [2]	294	330	362

[1] Characteristic of alpha and gamma forms of chlordane.

[2] These compounds are mixtures of various isomers.

Table 9.—*Acid Extractable Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
2-Chlorophenol	128	64	130	129	131	157
2-Nitrophenol	139	65	109	140	168	122
Phenol	94	65	66	95	123	135
2,4-Dimethylphenol	122	107	121	123	151	163
2,4-Dicholorphenol	162	164	98	163	165	167
2,4,6-Trichlorophenol	196	198	200	197	199	201
4-Chloro-3-methyl phenol	142	107	144	143	171	183
2,4-Dinitrophenol	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	198	182	77	199	227	239
Pentachlorophenol	266	264	268	267	265	269
4-Nitrophenol	65	139	109	140	168	122
Anthracene (d-10) [1]	188	94	80	189	217	

[1] Suggested internal standard.

Table 10.—*DFTPP Key Ions and Ion Abundance Criteria*

	Ion abundance criteria
Mass:	
51	30 to 60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40 to 60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5 to 9 percent of mass 198.
275	10 to 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 to 23 percent of mass 442.

BILLING CODE 6560-01-M

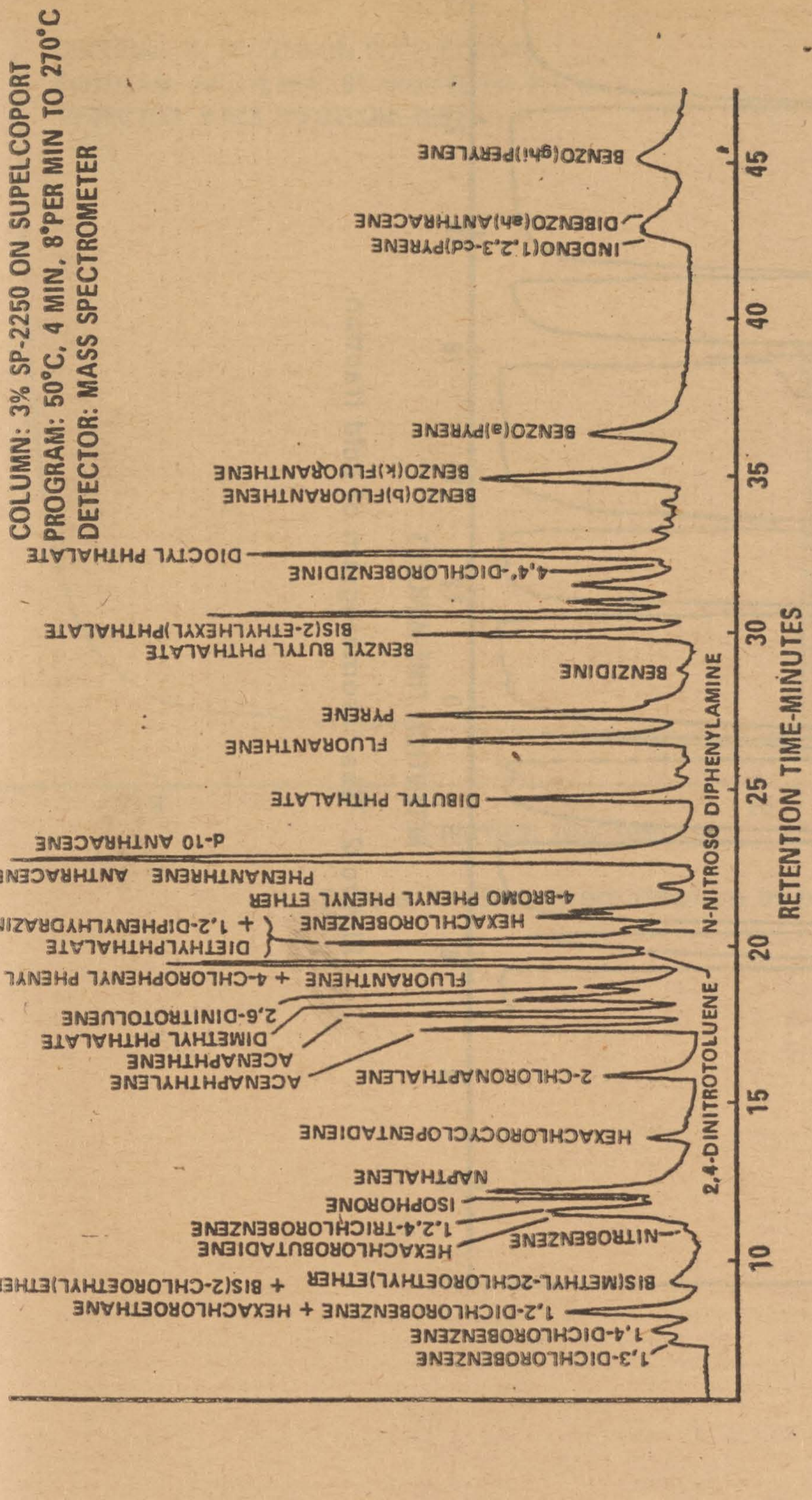


Figure 1. Gas chromatogram of base/neutral fraction

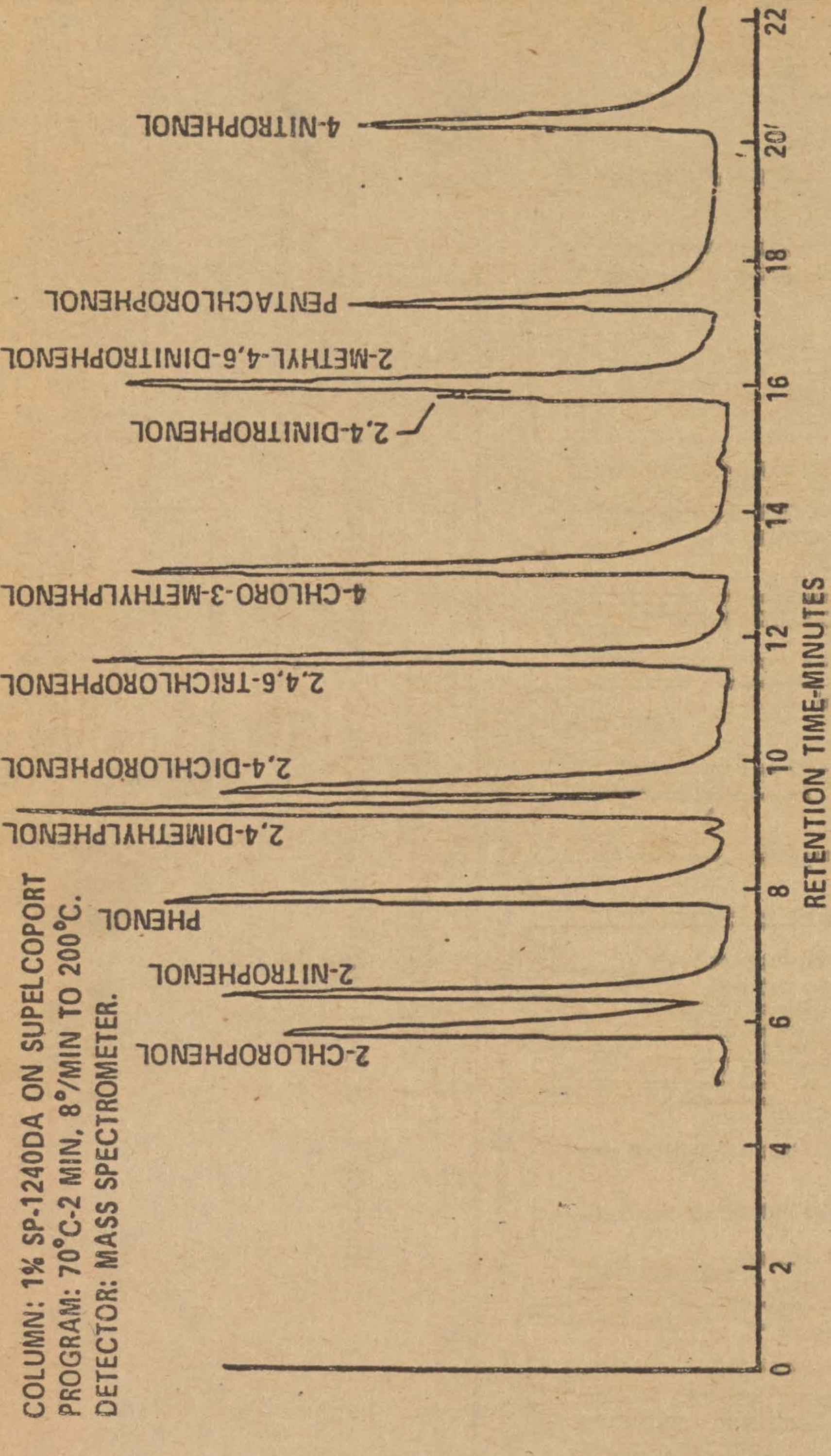


Figure 2. Gas chromatogram of acid fraction

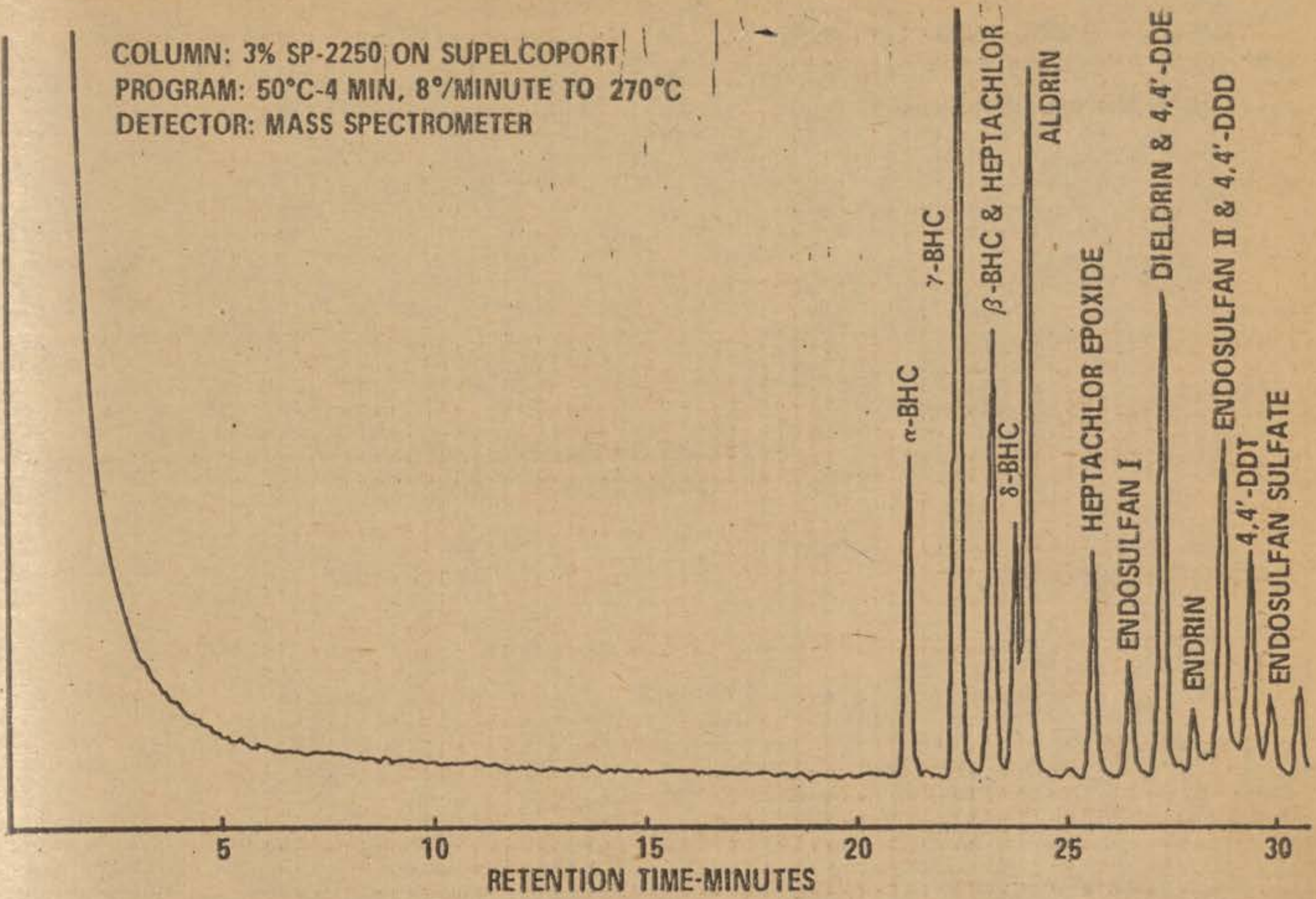


Figure 3. Gas chromatogram of pesticide fraction

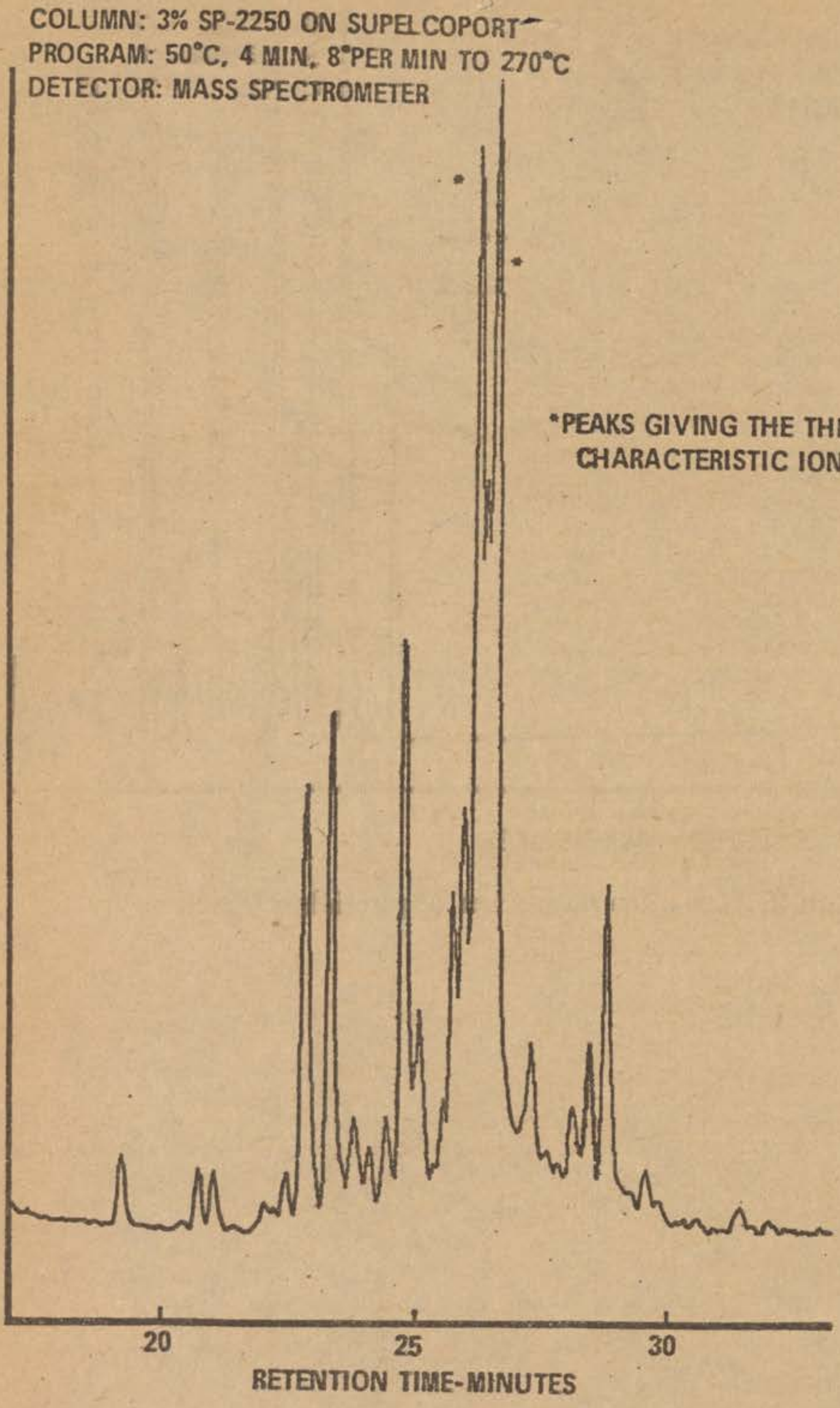


Figure 4. Gas chromatogram of chlordane

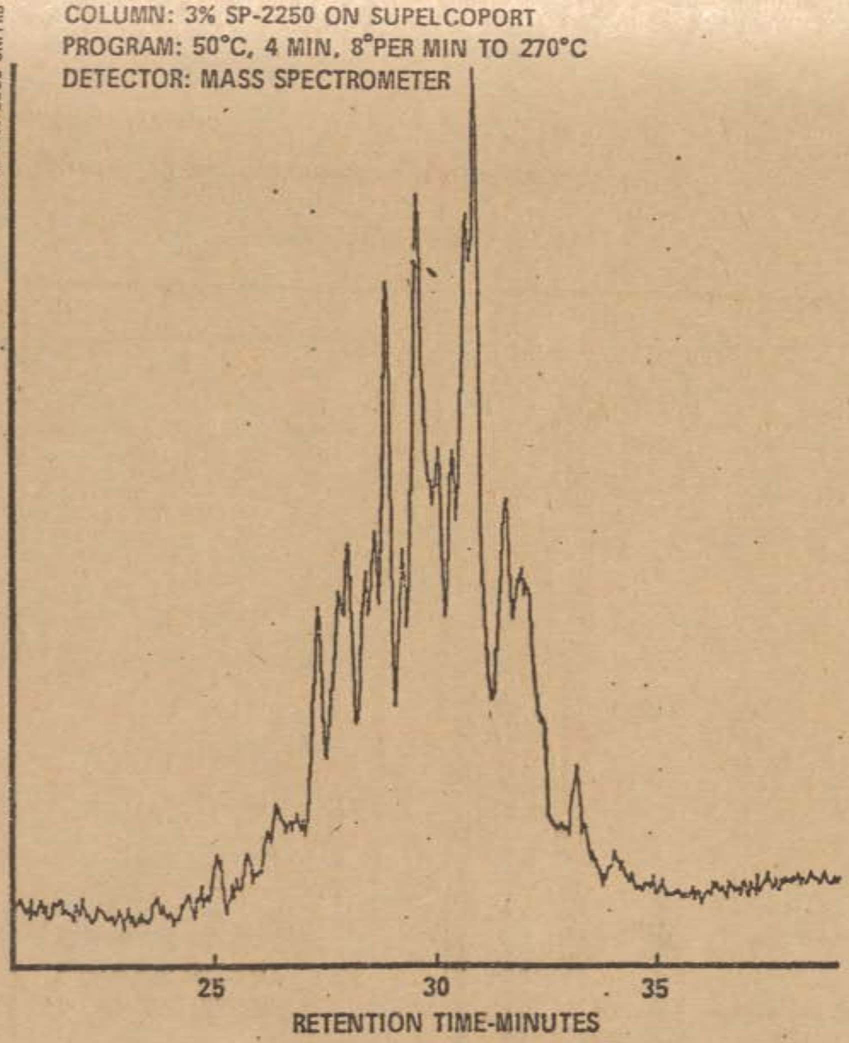


Figure 5. Gas chromatogram of toxaphene

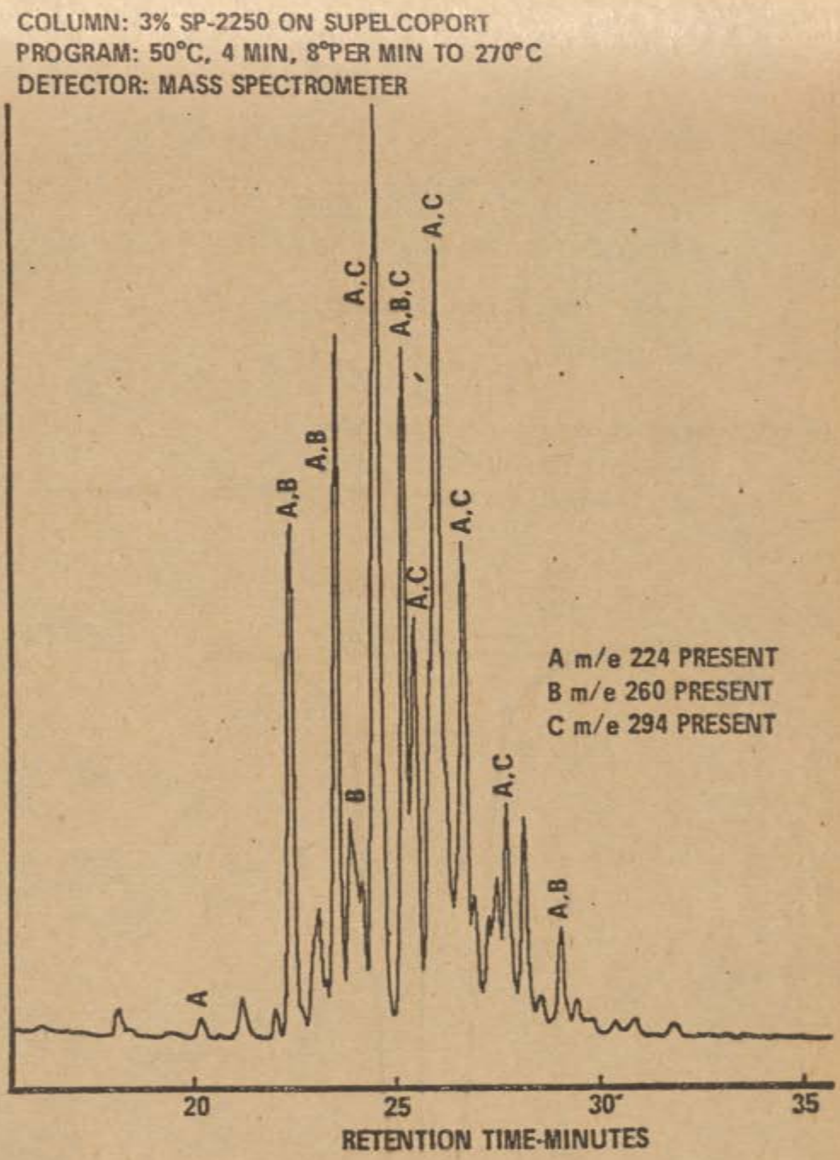
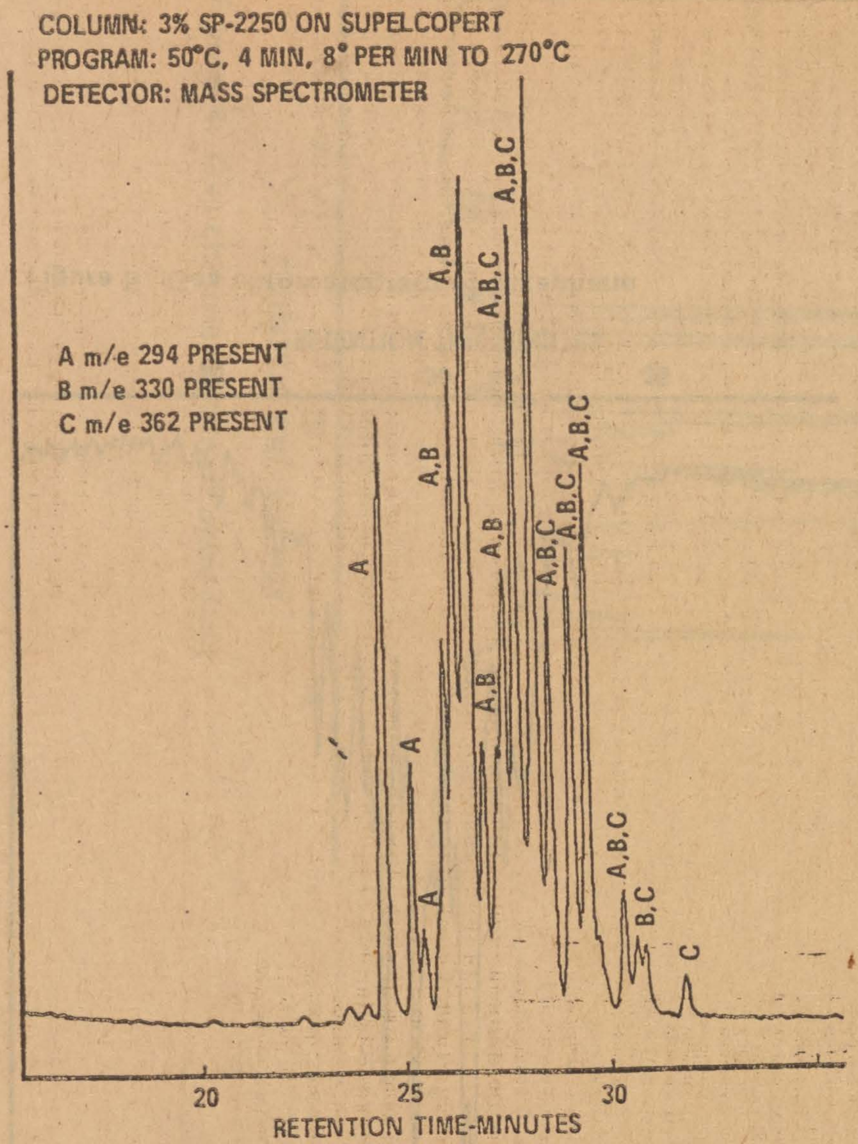


Figure 6. Gas chromatogram of Arochlor 1248

BILLING CODE 6560-01-C

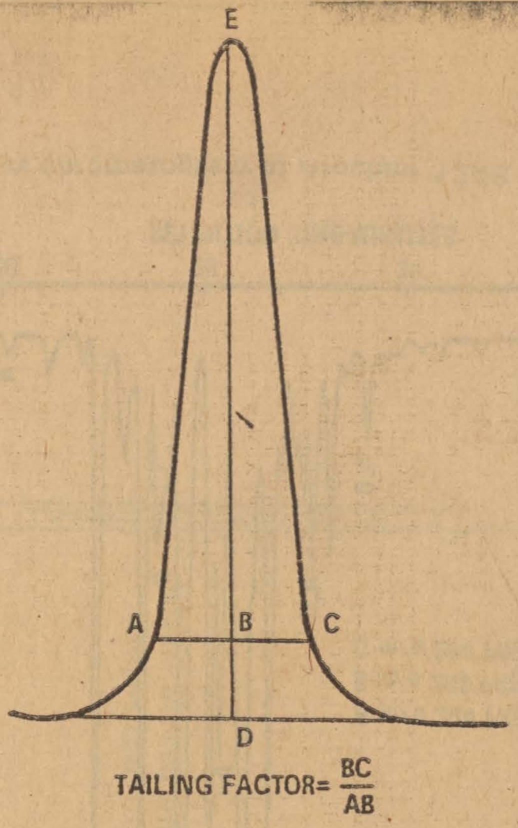


COLUMN: 3% SP-2250 ON SUPELCOPERT
PROGRAM: 50°C, 4 MIN, 8° PER MIN TO 270°C
DETECTOR: MASS SPECTROMETER

A m/e 294 PRESENT
B m/e 330 PRESENT
C m/e 362 PRESENT

Figure 7. Gas chromatogram of Arochlor 1254

BILLING CODE 6560-01-C



TAILING FACTOR= $\frac{BC}{AB}$

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 1. Tailing factor calculation

Appendix III—Example Quality Assurance and Quality Control Procedures for Organic Priority Pollutants

Example Quality Assurance and Quality Control Procedures for Analysis for Organic Priority Pollutants

110 *Scope.*

111 These procedures are provided for use by laboratories performing analyses using EPA Methods 624 and 625. To provide data with a known degree of reliability, a strong quality assurance and quality control program is presented. The procedures are designed to produce data with known precision and accuracy so that a determination of confidence can be placed in the data. Quality Assurance (QA) is the total program for assuring the reliability of the monitoring data. Quality control (QC) is the routine application of procedures for controlling the measurement process.

112 Initially, the methodology must be validated for each industrial subcategory being measured by the laboratory. The requirement for validation of each subcategory is based on the assumed unique nature of the wastewater associated with most of the subcategories. Since the effluent from treatment is to be used for setting control limits, it will be used to develop initial validation data for the method prior to routine sampling and analyses. A particular subcategory may not require verification analyses of all three fractions (Volatiles, Base/Neutrals, and Acids), or for all of the individual compounds, in which case, the method requires validation only for the fraction or the selected compounds of interest.

113 The results of the validation analyses will be used to provide information with which to judge a laboratory's ability to interpret and implement the method for each future sample in the industrial subcategory. Initial QC limits for precision and accuracy will be established using these results, and then used in subsequent analyses as control limits. A numerical example is given in Appendiix A.

114 After the method is validated for each subcategory and routine analysis begins, continuing QA/QC will be required to ensure that the subsequent analyses are within the established control limits.

115 Prior to developing initial method validation and a continuing quality control program, the analyst (individual or group if team approach is used) must demonstrate the ability to perform the required analyses. If a laboratory has not established precision and accuracy criteria for clean water, the laboratory must perform replicate analyses of clean water as prescribed in section 121.

120 *Routine Quality Assurance and Quality Control.*

121 *Preliminary Clean Water Precision and Accuracy.*

121.1 Before any work is begun on actual field samples, a laboratory must demonstrate its ability to properly perform the liquid-liquid extractions, the gas purge extractions, and the required chromatography. Clean water spikes are analyzed to demonstrate the laboratory's ability to implement Methods 624 and 625, and to establish the baseline precision and accuracy criteria for the method in that laboratory.

121.2 Procedure:

121.2.1 Prepare "organic-free" water for use in determining preliminary precision and accuracy according to the procedures given in Methods 624 and 625.

121.2.2 Spike four replicates of clean water with each compound of interest at a concentration approximately equal to 10 times the limit of detection. In addition, spike all purgeable aliquots with a minimum of three surrogate standards at a level of 100 μg/l. For extractable organics, each replicate must be one liter; each purgeable sample requires at least 100 ml. Do not dose purgeables with more than 20 μl of an alcoholic standard per each 100 ml of water. Analyze spiked solutions according to method 624 or 625.

121.3 Precision—For each parameter, use the resulting observed values of the spikes (O_1, O_2, O_3, and O_4) to calculate the standard deviation (S) of the replicates according to Equation 1.

$$\text{Eq. 1} \quad S = \sqrt{\frac{n\sum_{i=1}^{n} O_i^2 - (\sum_{i=1}^{n} O_i)^2}{n(n-1)}}$$

Where:

n=number of replicates

121.4 Accuracy—For each parameter, use the resulting observed values of the spikes (O_1, O_2, O_3, and O_4) to calculate the mean percent recovery

$$\text{Eq. 2} \quad \overline{P} = \frac{100\,\Big(\overset{n}{\underset{i=1}{}}\,O_i\Big)}{nT}$$

($\overline{P}$) of the method according to equation 2.

Where:

n=number of replicates

T=true value of the spike

121.5 The precision and accuracy data shall be documented for the record as evidence that the laboratory can properly perform the extractions and chromatography essential for methods 624 and 625.

122 *Method Blank*—The method blank is defined as an appropriate volume of "organic-free" water which has been processed exactly as the sample (including glassware, reagents, solvents, etc.). Reagents or solvents having background levels that interfere with the compounds to be determined must be purified and shown to be acceptable or replaced with some that are acceptable prior to proceeding with analyses. Problems encountered and corrective actions taken shall be documented and reported for the record.

122.1 For the extractable fractions (Base/Neutral or Acid), the method blank requires extraction of 1-liter "organic-free" water. A method blank must be extracted for each set of field samples extracted at a given time (at least one method blank per 20 field samples analyzed) and whenever a new source of reagent or solvent is introduced into the analytical scheme. The method blank can be screened by GC–FID. Analysis by GC–MS is required only if GC–FID analysis of the field blank gives any peaks larger than the internal standard peak.

122.2 For the volatile fraction, 5 ml of "organic-free" water should be analyzed by the purge and trap methodology only if positive interferences are noted during the analysis of a field blank. If positive interference still occurs, repeat the method blank analysis. If interference persists, dismantle the system, thoroughly clean all parts that contact the sample, purge gas and carrier gas. Replace or repack the sorbent trap and change purge and carrier gas.

123. *Field Blank*—The field blank is defined as an appropriate volume of "organic-free" water which has been

sent to the sampling site and back to the analytical laboratory in a container and bottle identical to the type used to collect the samples. Field blanks and samples must be shipped in separate containers. When received in the lab, the field blank is dosed, extracted and concentrated as if it were an actual sample.

123.1 For the extractable fractions (Base/Neutral or Acid), the field blank may be screened by GC–FID. Full GC–MS analysis is to be performed if the screening analysis gives any peaks larger than the internal standard peak.

123.2 For the volatile fraction, analyze a 5-ml field blank after each sample analysis. Follow the guidelines in 121.2 if positive interferences are noted during the analysis of a field blank.

130 *Method Validation.*

131 *Extractable Organics (Base/Neutrals-Acids)*—The following procedures are to be applied, separately, to samples being analyzed for the Base/Neutral-Acid group of compounds. The analyses shall be performed according to the procedures given in Method 625. The validation studies must be performed under the same conditions ordinarily applied to the samples of a given subcategory. That is, if separatory funnels are routinely used for extraction of the samples, the study must be conducted using separatory funnels. If continuous extractors are used for routine analysis of the subcategory, the validation study must be performed using the same type of continuous extractors.

131.1 Sample pretreatment—The laboratory should collect a sample of adequate volume to carry out the validation study and one field blank taken as described in the sampling protocol on the same day from the same source. Mix the sample and withdraw a 1-liter aliquot for analysis. Vigorously mix the sample with some type of stirring device. Withdraw aliquots, while stirring, into a 1-liter graduated cylinder, using a siphon made of glass or Teflon. Measure and record the volume. Transfer the aliquot to a 2-liter separatory funnel or continuous extractor for spiking. Initially analyze a 1-liter aliquot of the sample to determine the sample background so that proper spiking levels can be selected for 131.2.1. The remainder of the sample should be stored at 4° C until the validation study is begun. At the same time, analyze a 1-liter aliquot of the field blank. Choose three levels of compound spikes to cover the expected concentration range of the samples in the subcategory.

131.2 Preparation of Aliquots for Validation Study—Withdraw twelve 1-liter aliquots from the stirred composite sample as described in 131.1. Separate into three groups of four.

131.2.1 Spiking of Aliquots—Spike two aliquots of each group with surrogate standards only. The other two aliquots are spiked with surrogate standards plus the standard pollutant compounds of interest at one of the concentration levels (See Figure 2). Repeat this process for each group of aliquots. Select the three spiking concentrations for the compounds of interest based on the results of the background analysis obtained in 131.1. If the initial background level for a particular pollutant is x, select the three spiking levels to give final concentrations 2×, 10×, and 100×. If x equals 15 μg/l, dose with 15, 135, and 1485 μg per liter. This gives final concentrations of the pollutant of 30, 150, and 1500 μg/l. Spike each 1-liter replicate with each surrogate at a level of 100 μg/l.

Note.—Consideration should be given to the water solubility of the compounds being spiked when selecting the spiking concentration levels.

131.2.2 Prepare spiking standards in concentrations such that no more than 5 ml of spiking solution is added for each liter of sample. This will ensure that the solubility of the standard in water will not be significantly affected by the added organic solvent. Add the spiking solution to the sample aliquots in the separatory funnel using a transfer pipet. After adding the spikes, thoroughly mix the samples and after one hour at room temperature proceed with the extraction. If continuous extractors are used, it may be necessary to spike the 1-liter aliquots before they are placed into the extractor. Place the aliquot in a separatory funnel or a clean bottle, spike, and transfer to the extractor. The bottle must be rinsed with solvent. Wait an hour and begin the extraction.

131.3 Use of the Data from Spiked Samples in Analyses—The data obtained from the determination of pollutants of interest are used to calculate the precision and accuracy of the method and to establish control limits for the individual compounds of interest. Surrogate spikes are added to every sample to provide quality control on every sample by monitoring for matrix effects and gross sample processing errors. The surrogate is *not* used as an internal standard for quantification purposes. Suggested surrogate standards are given in Section 6.4 of Method 625. If validation is needed for only one fraction, only the surrogates for that fraction need be added.

131.4 Extract and analyse all aliquots as directed in Method 625 or other appropriate EPA methods.

131.5 Calculation of Precision and Accuracy—The precision of the method may be calculated from the data obtained during the validation study. There are three spiked concentration levels of pollutants as outlined in Figure 2. The method precision for the background level of pollutants occurring in the sample may be calculated from the three pairs of replicate aliquots which are spiked only with surrogate standards (A1, A2; B1, B2; C1, and C2. See Figure 2). The precision and accuracy for the surrogates may be calculated from all twelve replicates since the spiking level is constant for both sets of six samples. The precision and accuracy for the surrogates may be calculated for each set of six samples if there is an effect due to the added pollutant spike. Similarly, the precision and accuracy at each spike level of the pollutants of interest may be determined from the two replicate aliquots that received that spike (D1, D2; E1, E2; F1, and F2. See Figure 2).

a. *Precision.*

Calculate the range (R) for each pair of replicate aliquots i.e., duplicate analyses, according to equation 3:

Eq. 3 $R=|X_1 - X_2|$

Where:

X_1 and X_2 are each an analytical result from two replicate aliquots.

The concentration level related to R can be represented as in equation 4.

Eq. 4 $$X = \frac{(X_1 + X_2)}{2}$$

Where:

X is the mean of the duplicate analyses, X_1 and X_2.

For any group of n duplicate analyses that are considered similar to each other, their ranges (R_i) and means (X_i), where i = 1 to n, can be used to estimate the critical difference (R_c) between similar future duplicate analyses or any specific concentration level (C). Calculate R_c as shown in equation 5.

Eq. 5 $$R_c = \frac{3.27(C)}{n}\left[\sum_{i=1}^{n}\frac{R_i}{X_i}\right]$$

From these data develop a table of R_c values for various concentration (C) values that span the concentration range of interest. Use these initial critical difference values to judge the acceptability of succeeding duplicate results generated under the same conditions. Revise and update as additional duplicate data becomes available. When more than 15 pairs of duplicates are available within any specific concentration level C, R_c should be calculated directly from the average range of these duplicates alone. Equation 5 reduces to

$$R_c = \frac{3.27(C)}{n}\left[\sum_{i=1}^{n} R_i\right]$$

b. *Accuracy for Pollutants.* Calculate the background concentration of priority pollutants occurring in each of the field composite samples. The calculation is similar to equation 4, but there are six pieces of data (A1, A2, B1, B2, C1, C2) available for this calculation as shown in Figure 2. Therefore, the calculation is as shown in equation 6.

$$\text{Eq. 6} \qquad \bar{X} = \frac{\left(\sum_{i=1}^{6} X_i\right)}{6}$$

Where:

$\bar{X}$ is the mean X_i, i-1 to 6 are the analytical results for the six 1-liter aliquots of a single composite sample spiked with surrogates only.

Calculate the recovery of each pollutant in each of the 1-liter aliquots spiked with the pollutants of interest (D1, D2, E1, E2, F1 and F2) according to equation 7:

$$\text{Eq. 7} \qquad P = \frac{100\ (Z - X)}{T}$$

Where:

P is the percent recovery of the spike

Z is the analytically determined concentration of the pollutant in the spiked aliquot

$\bar{X}$ is the mean background concentration of the pollutant and

T is the true value of the spike.

Determine the percent recoveries for each pollutant of interest at all of its concentration levels. If there is no significant difference between the percent recoveries for the various concentration levels, all n of the percent recovery values may be treated together as in equations 8 and 9. If some of the percent recovery values are significantly different, each group of similar percent recoveries must be treated independently to develop its own characteristic mean percent recovery ($\bar{P}$) and its associated standard deviation (S_p)

$$\text{Eq. 8} \quad \bar{P} = \frac{\sum_{i=1}^{n} P_i}{n}$$

Where:

$\bar{P}$ is the mean percent recovery

P_i is an individual percent recovery value

n is the number of observations at this concentration level

$$\text{Eq. 9} \qquad S_p = \sqrt{\frac{n\sum_{i=1}^{n} P_i^2 - \left(\sum_{i=1}^{n} P_i\right)^2}{n\,(n-1)}}$$

c. *Accuracy for Surrogates.* Proceed exactly as with the pollutants of interest in 131.5b above, keeping the following two differences in mind: there is no background concentration and there are six sets of duplicate analyses for the surrogate spikes; three sets spiked with pollutants of interest (D1, D2; E1, E2; F1, F2) and three sets without (A1, A2; B1, B2; C1, C2), see Figure 2. Calculate the percent recovery as shown in equation 10.

$$\text{Eq. 10} \qquad P = \frac{100\ Z}{T}$$

Where:

P is the percent recovery of the surrogate spike.

Z is the measured value of the surrogate spikes in the aliquot.

T is the calculated or true value of the surrogate spikes added to the sample.

Calculate the mean percent recovery ($\bar{P}$) and the standard deviation (S_p) of the percent recovery of the surrogate spikes in all of the sample aliquots according to equations 8 and 9.

132 *Volatile Organics (Purgeables)*

132.1 The validation of the method for purgeables requires a minimum of 600 ml sample. The validation may be performed on a grab sample or a composite sample prepared from discrete grab samples.

Thirteen 5-ml aliquots of each sample are required. They should be treated and spiked according to Sections 132.2 d through f and 132.4.3. The remaining volume of sample is transferred to a clean container, i.e., vial or vials and sealed with no headspace as done when collecting a sample. This sample should be held at 4°C until it is determined that there is no further need for the sample. Figure 3 summarizes the validation study for volatile organics. Caution: Prepare only as many sample aliquots as can be analyzed in the working day. This may mean that each of the three concentration levels will be analyzed on different days.

132.2 Pretreatment of Grab Samples to be composited—Individual grab samples should be composited according to the following procedure:

a. Composite only grab samples of equal volume.

b. Carefully pour the contents of all individual grab samples collected from a given source during the specified time period into a 1000-ml round-bottom flask which is chilled in a wet ice bath.

c. Stir the mixture gently with a glass rod for approximately one minute while in the ice bath.

d. Carefully fill 13 clean 40-ml vials or three 120-ml vials and four 40-ml vials with composited sample.

e. Take one 40-ml vial for immediate analysis to determine the background of the purgeable pollutants.

f. Store the remaining vials at 4° C until the validation study is begun.

132.3 Spiking levels for pollutant and surrogate standards—The spiking levels of the pollutants are determined by the background (X) in the samples. The low level spike will give a final concentration that is 2 times the background level. The intermediate and high level spikes will give final concentrations that are 10 and 100 times the background level. Concentrations in excess of 1000 μg/l are likely to flood the gas chromatographic column. Therefore, the total concentration (background plus spike) of each individual pollutant should not exceed 900 μg/l. Even at this level, the solubility of the compounds in the sample must be considered. The spiking level for all surrogate standards should be 100 μg/l.

132.4 Spiking Procedures.

132.4.1 Preparation of Spiking Standards—Prepare methanolic stock standard solutions of the pollutants and the surrogate standards according to the directions given in Method 624.

From the methanolic primary dilutions prepare secondary aqueous spiking mixtures of the surrogate standards so that 20.0 μl of the primary standard solution, diluted to 50.0 ml in organic free water will permit adding 5 μl of the resulting solution to the 5 ml sample giving the desired surrogate concentration level of 100 μg/l.

Prepare spiking mixtures of the pollutant standards in methanol so that 20.0 μl of the solution added to 100.0 ml of sample will give the desired concentration levels.

132.4.2 To minimize the solubility effect of methanol on the constituents to be measured, do not inject more than 20 μl of spiking solution per 100 ml of sample. Never use a pipet to transfer samples or aqueous standards that are to be analyszed for volatile purgeable compounds. Transfer samples by pouring into the receiving vessel.

132.4.3 Spiking the Sample Aliquots—Take one of the 120-ml or 3 of the 40 ml sample aliquots from cold storage, equilibrate to room temperature, and fill a 100 ml volumetric flask to mark with the sample. Rapidly inject 20 μl of the methanolic solution of pollutant spiking standard (concentration 2X) into the expanded area of the flask below the neck. Stopper and mix by gently inverting the flask three times. Fill two 5-ml syringes with spiked sample from the flask as directed in the analytical protocol. Open the valve of the syringe and inject 5 μl of the surrogate standard spiking solution. Inject the sample aliquot into the purging device and analyze according to Method 624.

Take one of the 40-ml sample aliquots from cold storage, equilibrate to room temperature and fill two 5-ml syringes with the sample as directed in Method 624. Spike 5 μl of the surrogate standard water solution (concentration 100 μg/l) into the syringe through the valve giving a final concentration of 100 μg/l. Inject the sample aliquot into the purge device and analyze according to Method 624. See Figure 3. Repeat this procedure twice, giving three sets of analyses of two samples spiked with surrogate standards only and two samples spiked with surrogate standards and pollutant compounds of interest.

132.5 Calculation of Precision and Accuracy—The precision and accuracy for the purgeable pollutants and the surrogate standards are calculated as directed for the semivolatile solvent extractable compounds in paragraphs 131.5a, b, and c.

140 *Continuing Quality Assurance and Quality Control.*

141 *Extractable Organics (First Samples)*—The following procedures should be applied to the first sample of a subcategory for the Base/Neutral and Acid groups. An outline diagram for first sample ongoing quality assurance samples is given in Figure 4.

141.1 Withdraw three 1-liter aliquots of the composite sample according to the procedure in 131.1.

141.2 Spiking the Sample Aliquots—Spike one of the aliquots with pollutant standards plus the surrogate standards and two of the aliquots with surrogate standards only.

141.3 Add a spike sufficient to approximately double the background concentration of the priority pollutants as determined in 131.5b. If the original concentration is higher than the midpoint of the calibration curve, then the concentration of the spike should be approximately one-half the original concentration. Surrogate spikes as specified in 131.3 should be added to all three aliquots from each sample at a concentration level of 100 μg/1.

141.4 Analyze according to Method 625.

141.5 Calculations of Precision and Accuracy

a. For the first sample, calculate the precision of the duplicate analyses (X_1 and X_2) from the two 1-liter aliquots for the pollutants background and the surrogate standards. Calculate the range (R) of the results according to equation 11.

Eq. 11 $$R = |X_1 - X_2|$$

The concentration of each compound is represented by the mean of the duplicate values. Calculate the mean ($\overline{X}$) according to equation 12.

Eq. 12 $$X = \frac{(\bar{X}_1 + X_2)}{2}$$

Refer to the table of critical range values developed in 131.5a, to find the concentration (C) nearest to X. Use this R_c to evaluate the acceptability of R from Eq. 11. If R is greater than R_c, the system precision is out of control and the source of this unusual variability should be identified and resolved before continuing with routine analyses. After correcting the source of this unusual variability, reanalyze the sample if possible. Record the results of all duplicate analyses and periodically (after 5 to 10 additional duplicate results are obtained), revise, update, and improve the table of critical range values.

b. *Accuracy for Surrogate Spikes.* Calculate the recovery of the surrogate spikes in the duplicates according to equation 13.

Eq. 13 $$P = \frac{100\ Z}{T}$$

Where:

P is the percent recovery.

Z is the analytically determined concentration of the surrogate standard spikes.

T is the true value of the surrogate standard spikes added in 132.4.3.

If the percent recoveries are not within the interval $P + 3S_p$ as determined in 131.5c, the system should be checked for problems. If problems exist, they must be resolved before continuing with routine analyses. Record the recovery of all surrogate spikes and periodically (every 5 to 10 additional data points), revise and update the recovery criteria.

c. *Accuracy for Priority Pollutant Spikes.* Using the results obtained from the 1-liter aliquot of composite sample spiked with surrogate standards and pollutant standards, calculate the recoveries of the priority pollutants according to equation 14.

Eq. 14 $$P = \frac{100\ (Z - \bar{X})}{T}$$

Where:

P is the percent recovery
Z is the analytically determined concentration of the pollutant spikes
T is the true value of the pollutant spikes added in 132.4.3, and
$\overline{X}$ is the mean concentration of the pollutant background determined by equation 9.

If the percent recovery is not within the interval of $P + 3S_p$, as determined in 131.5b the system should be checked for problems. If problems exist, they must be resolved before continuing with routine analyses. Record the recovery of all spikes and periodically revise and update the accuracy criteria.

142 *Extractable Organics—(Subsequent Samples)*—The following procedures should be applied to each subsequent sample of a subcategory of the Base-Neutral and Acid groups. A flow diagram for each subsequent ongoing quality assurance sample is given in Figure 5.

142.1 Withdraw a one-liter aliquot as directed in 131.1

142.2 Spike the aliquot with surrogate standards at a concentration of 100μg/l.

142.3 Analyze according to Method 625.

142.4 Determine the percent recovery of the surrogate standards using Equation 10. If the percent recovery is outside the interval $P + 3S_p$ as determined in 131.5c, the analytical system should be checked for problems. If problems exist, they must be resolved before continuing further sample analyses.

142.5 A field blank must be analyzed according to Method 625. If priority pollutants are found and quantified, the values for the field blank should be noted and reported along with sample results. If significant interference problems occur, the method blank must be analyzed to determine if interference was introduced in the field or the laboratory. Appropriate action musts be taken to eliminate the problem before continuing with the analysis of routine samples.

143 *Volatile Organics (First Sample)*—The following procedures should be carried out on the first sample from each subcategory. An outline is given in Figure 4.

143.1 If grab samples are to be composited, follow instructions given in Section 132.2 and 132.4.3. Prepare six 5-ml aliquots for analysis.

143.2 Spike two aliquots with the pollutant standards at a level twice that determined in Section 132.5 and the surrogate standards using the procedures in Section 132.3 and 132.4. Spike four 5-ml aliquots with surrogate standards only as in 132.3 and 132.4.

143.3 Analyze one of the duplicates spiked with pollutants and surrogate standards and two of the four replicates spiked with surrogate standards only. The remaining spiked aliquots are analyzed only if a problem is encountered with the analysis of the first set of aliquots.

143.4 Analyze the spiked aliquots according to Method 624.

143.5 Calculate the precision and accuracy as directed for the semivolatile solvent extractables as directed in 141.5.

144 *Volatile Organics (Subsequent Samples)*—The following procedures should be applied to each subsequent sample of the volatile organics group. An outline is given in Figure 5.

144.1 If grab samples are to be composited, follow the instructions given in Section 132.2 and 132.4.3. Prepare two 5-ml aliquots for analysis.

144.2 Spike both aliquots with surrogate standards only to give a concentration of 100 μg/l.

144.3 Analyze one of the aliquots according to Method 624. The other aliquot is analyzed only if a problem is encountered.

144.4 Determine the percent recovery of the surrogate standards using Equation 10. If the percent recovery is outside the interval $P \pm 3\ S_p$ as determined in 131.5c, then the analytical system should be checked for problems. If problems exist, they must be resolved before continuing further sample analysis.

144.5 Analyze a field blank representing the same day that the samples were collected. Follow the guidelines given in 142.5.

References

1. Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurements in Gas Chromatography-Mass Spectrometry Systems," *Anal. Chem. 47, 995–1000 (1975).*

2. McNair, H. M., and E. J. Bonelli, "Basic Gas Chromatography," p. 52, Consolidated Printing, Berkely, CA 1969.

Figure 2.—*Summary of Initial Validation Analyses for Extractable Samples*

	Liters used	GS/MS runs
1. Collect a minimum of 3½ gallons of sample		
2. Withdraw a 1-liter aliquot. Store composite at 4° C. Separate into three groups of 4 aliquots each	1	
3. Determine the background concentration (X) of each pollutant of interest.		1
4. Withdraw twelve 1-liter aliquots from the composite		
5. (a) Dose 2 of aliquots with surrogate standards only at 100 μg/l. Label as A1 and A2	2	
(b) Dose 2 aliquots with surrogate standard at 100 μg/l and pollutants of interest to give a concentration level of 2X. Label as D1 and D2	2	
(c) Analyze A1, A2, D1, and D2 using Method 625		4
6. Repeat 5a, b, and c. Label surrogate standards only as B1 and B2. Use 10X level for priority pollutants. Label as E1 and E2	4	4
7. Repeat 5a, b, and c. Label surrogate standards only as C1 and C2. Use 100X level for priority pollutants of interest. Label as F1 and F2	4	4
Total	13	13

Figure 3.—*Summary of Initial Validation Analyses for Purgeable Samples*

	5-ml syringes used	GC/MS runs
1. Collect a minimum of 600 ml of sample		
2. Fill 13 clean 40-ml vials or 3 clean 120-ml vials + 4 clean 40-ml vials with composite, cap, and store at 4° C.		
3. (a) Fill a 5-ml syringe from one 40-ml vial	1	
(b) Analyze and determine the background concentration (X) of each priority pollutant		1
4. (a) Fill two 5-ml syringes from one 40-ml vial	2	
(b) Dose with surrogate standards at 100 μg/l. Label as A1 and A2.		
(c) Analyze A1 and A2 using Method 624		2
(d) Fill a 100 ml volumetric to mark using one 120-ml or three 40-ml vials		
(e) Dose with 20 μl of pollutants of interest to give a concentration of 2X		
(f) Fill two 5-ml syringes from the 100-ml volumetric	2	
(g) Dose each syringe with surrogate standards at a concentration of 100 μg/l. Label as D1 and D2		
(h) Analyze D1 and D2 using Method 624		2
5. Repeat 4. Label surrogates only as B1 and B2. Use 10X level for pollutant of interest. Label priority pollutants plus surrogate standards as E1 and E2	4	4
6. Repeat 4. Label surrogates only as C1 and C2. Use 100X level for pollutant of interest. Label priority pollutants as F1 and F2	4	4
Total	13	13

Figure 4.—*Summary of Ongoing Quality Assurance for First Sample*

Extractables	Liters used	GC/MS runs
1. Composite the Sample		
2. (a) Withdraw three 1-liter aliquots	3	
(b) Dose two aliquots with surrogate standards only at 100 μg/l		
(c) Dose one aliquot with surrogate standards and the pollutants of interest to give a concentration of 2X, Section 131.5		
(d) Analyze using Method 625		3
Total	3	3

Purgeables	5 ml syringes used	GC/MS runs
1. Composite the Sample		
2. (a) Fill 4 clean 4-ml vials or 1 clean 120-ml vial + 1 clean 40-ml vial with composite. Store at 4° C		
3. (a) Fill four 5-ml syringes from one 40-ml vial	4	
(b) Dose each with surrogate standards at 100 μg/l		
(c) Fill a 100 ml volumetric to mark using the 120-ml vial or three 40-ml vials		
(d) Dose with 20 μl of pollutants of interest to give a concentration of 2X, Section 132.5		
(e) Fill two 5-ml syringes from the 100 ml volumetric	2	
(f) Analyze two 5-ml syringes containing surrogate standards only and one 5-ml syringes containing surrogate standards and pollutants of interest using method 624		3
Total	6	3

Figure 5.—*Summary of Ongoing Quality Assurance for Subsequent Samples*

Extractables	Liters used	GC/MS runs
1. Composite the Sample		
2. (a) Withdraw a 1-liter aliquot	1	
(b) Dose with surrogate standards only at 100 μg/l		
(c) Analyze using Method 625		1
Subtotal	1	1
Total (x29 days)	29	*29

Purgeables	5 ml Syringes used	GC/MS runs
1. Composite the Sample		
2. (a) Fill two 5-ml syringes with composite	2	
(b) Dose with surrogate standards at 100 μg/l		
(c) Analyze one 5-ml sample		1
Subtotal	2	1
Total (x29 days)	58	*29

*Assuming that field blank shows no pollutant of interest. If field blank were to be analyzed by GC/MS each subsequent day, the total would be 58.

Appendix A.—*Numerical Example of Validation Phase Results*

The following is an example of the calculations and results of a validation study.

	Surrogate standard (μg/l)				
Sample	Added	Found	Range (Eq. 3)	Mean (Eq. 4)	Percent recovery (Eq. 10)
A1	95	93			98
A2	95	97	4	95	102
B1	95	96			101
B2	95	98	2	97	103
C1	95	90			95
C2	95	94	4	92	99
D1	95	99			104
D2	95	95	4	97	100
E1	95	89			94
E2	95	91	2	90	96
F1	95	94			99
F2	95	96	2	95	101

Critical Difference (Eq. 5) $R_c=9.8$ at 95 μg/l.

Mean % Recovery (Eq. 8) P=99%.

Standard Dev. of P (Eq. 9) $S_p=3.1$; $3S_p=9.4$.

Acceptable Range of Recovery 90 to 100%.

During the same validation study, the following data were obtained for one of the priority pollutants studied.

Pollutant of interest								
Sample	Background	Added	Found	Range (Eq. 3)	Percent mean (Eq. 4)	Mean recovery (Eq. 7)	Recovery (Eq. 8)	Std. dev. (Eq. 9)
X	X	0	12					
A1	X	0	9					
A2	X	0	11	2	10			
B1	X	0	11					
B2	X	0	14	3	12.5			
C1	X	0	13					
C2	X	0	14	1	13.5			
D1	12	12	17			42		
D2	12	12	18	1	17.5	50	46	5.9
E1	12	110	102			82		
E2	12	110	107	5	106	86	84	3.3
F1	12	1200	1160			96		
F2	12	1200	1140	20	1150	94	95	1.2

Critical Difference (Eq. 5) for priority pollutants:

$R_c=6.7$ at 12 μg/l
$R_c=3.3$ at 17.5 μg/l
$R_c=16.4$ at 106 μg/l
$R_c=65$ at 1150 μg/l

Mean Value of X (Eq. 6):

X=12.0 μg/l (background concentration)

Is there a significant difference in the recoveries between the 100X and 10X levels? Apply a two tailed student's t-test with a confidence level of 95%.

$S_d=\sqrt{S^2_{100}+S_{10}^2}=\sqrt{(1.2)^2+(3.3)^2}=3.51$ (2 degrees of freedom)

$\bar{d}=X_{100}-X_{10}=95-84=TT$
$t_{exp}=d/S_d=11/3.5T=3.70$

Since 3.7 is less than 4.3 (t-value, 0.95, 2 degrees of freedom) there is no significant difference between the 100X and 10X levels. Apply equations 8 and 9 to the four recoveries for these two levels. The mean recovery (eq. 8) is 89% with a standard deviation (eq. 9) of 6.5 (3 degrees of freedom). Test the 2X level against this mean recovery and standard deviation.

$S_d=\sqrt{(6.5)^2+(5.9)^2}=8.78$ (4 degrees of freedom)

$\bar{d}=89-46=43$
$t_{exp}=43/8.78=4.90$

Since 4.90 is greater than 2.78 (t-value, 0.95, 4 degrees of freedom) there is a significant difference between the 2X and the 100X, 10X levels.

	2X	100X, 10X
Mean % Recovery (Eq. 8)	46	≈ 89
Standard deviation (Eq. 9)	5.9	6.5
$3S_p$	18	20
Acceptable Range (%)	28 to 64	69 to 109

For the first sample of the subcategory the following data were obtained.

	Surrogate std. (μg/l)			Priority pollutant (μg/l)		
Sample	Added	Found	Recovery (Eq. 13)	Added	Found	Percent recovery (Eq. 14)
a	100	93	93	0	13	
b	100	90	90	0	15	
c	100	105	105	12	20	50

For the Surrogate Standards, the range between a and b (Eq. 11) is 3, and the mean concentration (Eq. 12) is 91.5 μg/l. Since the critical difference is 9.8 at 95 μg/l, this range is acceptable. The recoveries of the Surrogate Standards in a, b, and c (Eq. 3) are all in the acceptable range of 90 to 109%. Therefore, the accuracy is acceptable.

For the pollutants of interest, the range between a and b is acceptable (less than 6.7), and the recovery is acceptable (acceptable range of 28 to 64%).

The following is an example of the results for samples 2 to 30 of a 30 sample study:

Pollutant (µg/l)		Surrogate standard (µg/l)			
Sample	Found	Added	Found	Percent recovery	
2	14	100	90	90	
3	15	100	99	99	
4	20	00	100	100	
5	11	100	107	107	
6	17	100	100	100	Update recovery for SS.*
7	18	100	100	100	
8	10	100	75	75	Not acceptable, disregard results.
9	14	100	92	92	
10	13	100	93	93	
11	12	100	94	94	Update recovery for SS.**
12	20	100	95	95	
30	15	100	95	95	Give final statistic on recovery of SS.

*Includes 20 results, 12 validation, 3 first day and days 2 through 6. Mean=99. Std. Dev.=4.6. Acceptable range 85–113%.

**Includes 25 results; day 8 result not included. Mean=98. Std. Dev.=4.6. Acceptable range 84–112%.

Appendix IV.—Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) for Trace Element Analysis of Water and Wastes

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

Interim

U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268

October 1979.

Foreword

This method has been prepared by the staff of the Environmental Monitoring and Support Laboratory—Cincinnati, with the cooperation of the EPA–ICP Users Group. Their cooperation and support is gratefully acknowledged.

This method represents the current state-of-the-art, but as time progresses, improvements are anticipated. Users are encouraged to identify problems and assist in updating the method by contacting the Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

Inductively Coupled Plasma (ICP) Optical Emission Spectrometric Method for Trace Element Analysis of Water and Wastes

1. Scope and Application.

1.1 This method may be used for the determination of dissolved, suspended, or total elements in surface water, drinking water, and domestic and industrial wastewaters.

1.2 Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken to ensure that potential interference are taken into account when dissolved solids exceed 1500 mg/l. (See 4.2)

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.

1.4 Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits. 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.

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 instructions provided by the manufacturer of the particular instrument.

Table 1—*Recommended Wavelengths* [1] and Estimated Instrumental Detection Limits

Element	Wavelength, nm	Estimated detection limit, µg/l [2]
Aluminum	308.2	45
Arsenic	193.7	53
Barium	455.5	2
Beryllium	313.0	0.3
Boron	249.8	5
Cadmium	226.5	4
Calcium	317.9	10
Chromium	267.7	7
Cobalt	228.6	7
Copper	324.7	6
Iron	259.9	7
Lead	220.3	42
Lithium	670.7	4
Magnesium	279.1	30
Manganese	257.6	2
Molybdenum	202.0	8
Nickel	231.6	15
Potassium	766.4	see [3]
Selenium	196.0	75
Silica (SiO_2)	288.1	27
Silver	328.0	7
Sodium	589.0	29
Strontium	407.7	0.5
Vanadium	292.4	8
Zinc	213.8	2

[1] The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can proved the needed sensitivity and are treated with the same corrective techniques for spectral interference. (See 4.1.1).

[2] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Optical Emission Spectroscopy Prominent Lines," EPA-600/4-79-017. Detection limits are sample dependent and as the sample matrix varies, these concentration values may also vary.

[3] Highly dependent on operating conditions and plasma position.

2. Summary of Method.

2.1 The method describes a technique for the simultaneous of 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. Additional interferences named in 4.1 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 8.3), or the sum of the dissolved plus suspended concentrations (Section 8.1 plus 8.2).

3.4 *Total recoverable*—The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid (Section 8.4).

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. funtional relationship between emission intensity and concentration.

3.7 *Instrument check standard*—A multielement standard of known concentrations prepared by the analyst. Should be included in the analytical scheme with a frequency of 10%. (See 6.6.1.)

3.8 *Reference standard*—A solution obtained from an outside source having known, verified values. Must be used initially to verify the calibration standards and analyzed thereafter as a blind sample on a weekly frequency. (See 6.6.2.)

3.9 *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 6.4.)

3.10 *Linear dynamic range*—The concentration range over which the analytical curve remains linear.

3.11 *Reagent blank*—A volume of deionized, distilled water containing the same acid matrix as the calibration standards carried through the entire analytical scheme. (See 6.5.2.)

3.12 *Calibration blank*—A volume of deionized, distilled water acidified with HNO_3 and HCl. (See 6.5.1.)

3.13 *Method of standard addition*—The standard addition technique involves the use of the unknown and the unknown plus a known amount of standard. (See 9.6.1.)

4. Interferences.

4.1 Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

4.1.1 *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 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.

4.1.2 *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. (See Note 1.) If these types of interferences are operative, they must be reduced by dilution of the sample and/or utilization of standard addition techniques.

Note 1.—The use of a peristaltic pump may lessen these interferences.

4.1.3 *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.

4.2 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 4.2.1 through 4.2.4, 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.

4.2.1 *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 (13.3) that has been established for that matrix). If not, a chemical or physical interference effect should be suspected.

4.2.2 *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 an alternate wavelength or comparison with an alternate method is recommended (See 4.2.3).

4.2.3 *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.

4.2.4 *Wavelength scanning of analyte line region*—If the appropriate equipment is available, wavelength scanning can be performed to detect potential spectral interferences.

5. Apparatus.

5.1 Inductively Coupled Plasma (ICP) Optical Emission Spectrometer.

5.1.1 Computer controlled atomic emission spectrometer with background correction.

5.1.2 Radiofrequency generator.

5.1.3 Argon gas supply, welding grade or better.

5.2 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.

6. Reagents and standards.

6.1 Acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent. Redistilled acids are acceptable.

6.1.1 *Acetic acid,* conc. (sp gr 1.06).

6.1.2 *Aqua regia:* Mix cautiously 3 parts conc. HCl (sp gr 1.19) and 1 part conc. HNO_3 (sp gr 1.41) just before use.

6.1.3 *Hydrochloric acid,* conc. (sp gr 1.19).

6.1.4 *Hydrochloric acid,* (1+1): Add 500 ml conc. HCl (sp gr 1.19) to 400 ml deionized, distilled water and dilute to 1 liter.

6.1.5 *Nitric acid,* conc. (sp gr 1.41).

6.1.6 *Nitric acid,* (1+1): Add 500 ml conc. HNO_3 (sp gr 1.41) to 400 ml deionized, distilled water and dilute to 1 liter.

6.2 *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.

6.3 *Standard stock solutions* may be purchased or prepared from ultra high purity grade chemicals or metals

(Caution: See Note 2). All salts must be dried for 1 h at 105° C unless otherwise specified.

Note 2.—Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow:

6.3.1 *Aluminum solution, stock,* 1 ml=100 μg Al: Dissolve 0.100 g of aluminum metal in an acid mixture of 4 ml of (1+1) HCl and 1 ml of conc. HNO_3 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.

6.3.2 *Arsenic solution, stock,* 1 ml=100 μg As: Dissolve 0.1320 g of As_2O_3 in 100 ml of deionized, distilled water containing 0.4 g NaOH. Acidify the solution with 2 ml conc. NHO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.3 *Barium solution, stock,* 1 ml=100 μg Ba: Dissolve 0.1516 g $BaCl_2$ 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.

6.3.4 *Beryllium solution, stock,* 1 ml=100 μg Be: Dissolve 1.127 g $Be_4O(C_2H_3O_2)_6$, beryllium acetate basic, in a minimum amount of conc. acetic acid. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.5 *Boron solution, stock,* 1 ml=100 μg B: Dissolve 0.5716 g anhydrous H_3BO_3 in deionized, distilled water and dilute to 1,000 ml. Because H_3BO_3 loses weight on drying at 105° C, use a reagent meeting ACS specifications and keep the bottle tightly stoppered to prevent the entrance of atmospheric moisture.

6.3.6 *Cadmium solution, stock,* 1 ml=100 μg Cd: Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.7 *Calcium solution, stock,* 1 ml=100 μg Ca: Suspend 0.2498 g $CaCO_3$ dried at 180° C for 1 h before weighing in deionized, distilled water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.8 *Chromium solution, stock,* 1 ml=100 μg Cr: Dissolve 0.1923 g of CrO_3 in deionized, distilled water. When solution is complete, acidify with 10 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.9 *Cobalt solution, stock,* 1 ml=100 μg Co: Dissolve 0.1407 g Co_2O_3 in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.10 *Copper solution, stock,* 1 ml=100 μg Cu: Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.11 *Iron solution, stock,* 1 ml=100 μg Fe: Dissolve 0.1430 g Fe_2O_3 in 10 ml deionized, distilled water with 1 ml (1+1) HCl. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.12 *Lead solution, stock,* 1 ml=100 μg Pb: Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.13 *Lithium solution, stock,* 1 ml=100 μg Li: Dissolve 0.5323 g Li_2CO_3, slowly in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.14 *Magnesium solution, stock,* 1 ml=100 μg Mg: Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.15 *Manganese solution, stock,* 1 ml=100 μg Mn: Dissolve 0.5225 g $Mn(NO_3)_2 \leqslant 6H_2O$ (do not dry) in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.16 *Molybdenum solution, stock,* 1 ml = 100 μg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in deionized, distilled water and dilute to 1,000 ml.

6.3.17 *Nickel solution, stock,* 1 ml = 100 μg Ni: Dissolve 0.4953 g $Ni(NO_3)_2 \leqslant 6H_2O$ in deionized, distilled water. Add 10 ml of conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.18 *Potassium solution, stock,* 1 ml = 100 μg K: Dissolve 0.1907 g KCl, dried at 110° C, in deionized, distilled water dilute to 1,000 ml.

6.3.19 *Selenium solution, stock,* 1 ml = 100 μg Se: Dissolve 0.1727 g H_2SeO_3 in deionized, distilled water and dilute to 1,000 ml.

6.3.20 *Silica solution, stock,* 1 ml = 100 μg SiO_2: *Do not dry.* Dissolve 0.4730 g $Na_2SiO_3 \leqslant 9H_2O$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.21 *Silver solution, stock,* 1 ml = 1 μg Ag: Dissolve 0.1575 g $AgNO_3$ in 100 ml of deionized, distilled water and 10 ml conc. HNO_3. Dilute to 1,000 ml with deionized, distilled water.

6.3.22 *Sodium solution, stock,* 1 ml = 100 μg Na: Dissolve 0.2542 g NaCl in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.23 *Strontium solution, stock,* 1 ml = 100 μg Sr: Dissolve 0.2416 g $Sr(NO_3)_2$ in deionized, distilled water. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.24 *Vanadium solution, stock,* 1 ml = 100 μg V: Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.3.25 *Zinc solution, stock,* 1 ml = 100 μg Zn: Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 ml conc. HNO_3 and dilute to 1,000 ml with deionized, distilled water.

6.4 *Mixed calibration standard solutions*—Prepared mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks. (See 6.4.1 thru 6.4.6) Add 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl and dilute to 100 ml with deionized, distilled water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference. Care should be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to a TFE fluorocarbon bottle for storage. Fresh mixed standards should be prepared weekly. Some typical combinations follow:

6.4.1 *Mixed standard solution I*—Iron, manganese, cadmium, lead, and zinc.

6.4.2 *Mixed standard solution II*—Beryllium, copper, strontium, vanadium, and cobalt.

6.4.3 *Mixed standard solution III*—Molybdenum, silica, lithium, and barium.

6.4.4 *Mixed standard solution IV*—Calcium, magnesium, sodium, and potassium.

6.4.5 *Mixed standard solution V*—Aluminum, arsenic, boron, chromium, nickel, and selenium.

6.4.6 *Mixed standard solution Vi*—Silver.

6.5 Two types of blanks are required for the analysis. The calibration blank (3.12) is used in establishing the analytical curve while the reagent blank (3.11) is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

6.5.1 *The calibration blank* is prepared by diluting 2 ml of (1+1) HNO_3 and 2 ml of (1+1) HCl to 100 ml with deionized, distilled water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

6.5.2 *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.

6.6 In addition to the calibration standards, an instrument check standard (3.7) and a reference standard (3.8) are also required for the analyses.

6.6.1 *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. This standard should be included in the analytical scheme with a frequency of 10%.

6.6.2 *The reference standard* should be prepared according to the instructions provided by the supplier. Following initial verification of the calibration standards, analyze weekly.

7. Sample handling and preservation.

7.1 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 linear polyethylene, polyproplyene or TFE-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 3 and 4).

Note 3.—*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 4.—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.

7.2 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.

7.2.1 For the determination of dissolved elements the sample must be filtered through a 0.45-μm membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus is 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.

7.2.2 For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45-μm 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.

7.2.3 For the determinaion of total or total recoverable elements, the sample is acidified with 5 ml conc. HNO_3 per liter (pH 2) as soon as possible, preferably at the time of collection. The sample is not filtered before processing.

8. Sample Preparation.

8.1 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. 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 8.3.

8.2 For the determinaton of suspended elements, transfer the membrane filter containing the insoluble material to a 250-ml Griffin beaker and add 3 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 (DO NOT BAKE), cool, add 2 ml of (1+1) HNO_3 and 2 ml HCl (1+1) per 100 ml dilution and warm the beaker gently to dissolve any soluble material. 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. Adjust the volume based on the expected concentrations of elements present. This volume will vary depending on the elements to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended."

8.3 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. (DO NOT BAKE.) Cool the beaker and add another 3 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 gentle 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 2 ml of 1+1 HNO_3 and 2 ml of 1+1 HCl per 100 ml of final solution and warm the beaker to dissolve any precipitate or residue resulting from evaporation. 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. Adjust the volume based on the expected concentrations of elements present. The sample is now ready for analysis. Concentrations so determined shall be reported as "total."

Note 5.—If low determinations of boron are critical, quartz glassware should be used.

8.4 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 1 ml of HNO_3 (1+1) and 2 ml of HCl (1+1) to the sample and heat on a steam bath or hot plate until the volume has been reduced to 15–20 ml making certain the sample does not boil. After this treatment the sample is filtered to remove insoluble material that could clog the nebulizer, and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total."

9. Procedure.

9.1 Set up instrument with proper operating parameters established in Section 5.2. Instrument must be allowed to stabilize for at least 30 min prior to operations.

9.2 Initiate appropriaate operating configuration of computer.

9.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Section 6.4. Flush the system with the calibration blank (6.5.1) between each standard. (See note 6.) (The use of the average intensity of multiple exposures for both standardization and sample analysis has been found to reduce random error.)

NOTE 6.—For boron concentrations greater than 500 μg/l extended flush times of 1 to 2 minutes may be required.

9.4 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 2 percent (or the established control limits). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

9.5 Begin the sample run flushing the system with the calibration blank (6.5.1) between each sample. (See Note 6.) Analyze an instrument check standard (6.6.1) each 10 samples.

9.6 If it has been found that methods of standard addition are required, the following procedure is recommended.

9.6.1 The standard addition technique (13.2) 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 intererence 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 standared 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_s 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.

10. Calculation.

10.1 Reagent blanks (6.5.2) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

10.2 If dilutions were performed, the appropriate factor must be applied to sample values.

10.3 Results should be reported to the nearest μg/l, up to three significant figures, except calcium, magnesium, sodium, and potassium which are reported to the nearest 0.1 mg/l.

11. Quality Control (Instrumental).

11.1 Check the instrument standardization by analyzing appropriate quality control check standards as follow:

11.1.1 Analyze the instrument check standard (6.6.1) made up of all the elements of interest at a frequency of 10%. This check standard is used to determine instrument drift. If agreement is not within ± 2% of the expected values or within the established control limits, the analysis is out of control.

11.1.2 For the purpose of verifying interelement and/or background correction factors, analyze a second check standard, prepared in the following manner. Select a representative sample which contains minimal concentrations of the elements of interest. Spike this sample with the analytes of interest at or near 100 μg/l. (For effluent samples of expected high concentrations, spike at an appropriate level.) Values should fall within the established control levels of 1.5 times the standard deviation of the mean value of the check standard. If not, repeat the standardization.

11.1.3 A reference standard (6.6.2) from an outside source, but having known concentration values, should be analyzed as a blind sample on a weekly frequency. Values should be within the established quality control limits. If not, prepare new stock standards.

12. *Precision and Accuracy.*

12.1 In an EPA round phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been dosed with various metal concentrates. Table II lists the true value, the mean reported value and the mean % relative standard deviation.

Table II.—*ICP Precision and Accuracy Data*

	Sample No. 1			Sample No. 2			Sample No. 3		
Element	True value μg/l	Mean reported value μg/l	Mean percent RSD	True value μg/l	Mean reported value μg/l	Mean percent RSD	True value μg/l	Mean reported value μg/l	Mean percent RSD
Be	750	733	0.2	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	16	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.

13. References.

13.1 Winge, R. K., V. J. Peterson, and V. A. Fassel, "Inductively Coupled Plasma-Optical Emission Spectroscopy: Prominent Lines, EPA-600/4-79-017.

13.2 Winefordner, J. D., "Trace Analysis: Spectroscopic Methods for Elements," *Chemical Analysis*, Vol. *46*, pp. 41-42.

13.3 Handbook for Analytical Quality Control in Water and Wastewater Laboratories, EPA-600/4-79-019.

13.4 Garbarino, J. R. and Taylor, H. E., "An Inductively-Coupled Plasma Optical Emission Spectrometric Method for Routine Water Quality Testing," Applied Spectroscopy *33*, No. 3 (1979).

13.5 "Methods for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.

Appendix V—Biological Oxygen Demand, Carbonaceous Method 405.1 (5 Days, 20° C)

Biochemical Oxygen Demand—Method 405.1 (5 Days, 20° C)

STORET No. 00310, Carbonaceous 80082

1. Scope and Application.

1.1 The biochemical oxygen demand (BOD) test is used for determining the relative oxygen requirements of municipal and industrial wastewaters. Application of the test to organic waste discharges allows calculation of the effect of the discharges on the oxygen resources of the receiving water. Data from BOD tests are used for the development of engineering criteria for the design of wastewater treatment plants.

1.2 The BOD test is an empirical bioassay-type procedure which measures the dissolved oxygen consumed by microbial life while assimilating and oxidizing the organic matter present. The standard test conditions include dark incubation at 20° C for a specified time period (often 5 days). The actual environmental conditions of temperature, biological population, water movement, sunlight, and oxygen concentration cannot be accurately reproduced in the laboratory. Results obtained must take into account the above factors when relating BOD results to stream oxygen demands.

1.3 To obtain values for only carbonaceous BOD, the procedure (2.2) for inhibiting the nitrogeneous oxygen demand using 2-chloro-6(trichloromethyl) pyridine should be used.

2. Summary of Method.

2.1 The sampe of waste, or an appropriate dilution, is incubated for 5 days at 20° C in the dark. The reduction in dissolved oxygen concentration during the incubation period yields a measure of the biochemical oxygen demand.

2.2 Nitrogenous oxygen demand is inhibited by adding approximately 10 mg of 2-chloro-6(trichloromethyl) pyridine to each BOD bottle prior to adding the sample (or diluted sample) for incubation. Results of samples treated with inhibitor are to be reported as Biochemical Oxygen Demand, Carbonaceous, Storet No. 80082.

3. Comments.

3.1 Determination of dissolved oxygen in the BOD test may be made by use of either the Modified Winkler with Full-Bottle Technique or the Probe Method in this manual.

3.2 Additional information relating to oxygen demanding characteristics of wastewaters can be gained by applying the Total Organic Carbon and Chemical Oxygen Demand tests (also found in this manual).

3.3 The use of 60 ml incubation bottles in place of the usual 300 ml incubation bottles, in conjunction with the probe, is often convenient.

4. Precision and Accuracy.

4.1 Eighty-six analysts in fifty-eight laboratories analyzed natural water samples plus an exact increment of biodegradable organic compounds. At a mean value of 2.1 and 175 mg/l BOD, the standard deviation was ±0.7 and ± 26 mg/l, respectively (EPA Method Research Study 3).

4.2 There is no acceptable procedure for determining the accuracy of the BOD test.

5. References

5.1 The procedure to be used for this determination is found in: "Standard Methods for the Examination of Water and Wastewater, 14th edition," p. 543, Method 507 (1975).

5.2 Young, J. C., "Chemical Methods for Nitrification Control," J. Water Poll. Control Fed., *45*, p. 637 (1973).

507 Oxygen Demand (Biochemical)

1. Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test measures the oxygen required for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless oxidation of nitrogenous compounds is prevented by an inhibitor.

The method consists of placing a sample in a full, air-tight bottle and incubating the bottle under specified conditions for a specific time. Dissolved Oxygen (DO) is measured initially and after incubation. The difference in DO is the oxygen used and from it the BOD can be computed.

The bottle size, incubation temperature, and incubation period are all specified. Because most wastewaters contain more oxygen-demanding materials than the quantity of DO in oxygen-saturated water, it is necessary to dilute the sample before incubation to bring the oxygen required and oxygen supply into appropriate balance. Because bacterial growth requires such nutrients as nitrogen, phosphorus, and trace metals, these are added to the dilution water which is buffered to ensure that the pH of the incubated bottle remains in a range suitable for bacterial growth. Complete stabilization of a sample may require a period of incubation too long for practical purposes; therefore, the 5-day period has been accepted as standard.

Measurements of BOD that include both carbonaceous oxygen demand and nitrogenous oxygen demand generally are not useful; therefore, where appropriate, may be an inhibiting chemical used to prevent nitrogenous oxidation. Carbonaceous and nitrogenous demands are measured separately for predicting oxygen suppression in receiving streams and oxygen requirements for treatment plant design and operation.

The inclusion of ammonia in the citation water demonstrates that there is no intent to include the oxygen demand of reduced forms of nitrogen in the BOD test. If this ammonia were oxidized, errors would result because the oxygen use would not be due exclusively to pollutants in the sample.

The extent of oxidation of nitrogenous compounds during the 5-day incubation period depends on the presence of micro-organisms capable of carrying out this oxidation. Such organisms usually are not present in raw sewage or primary effluent in sufficient numbers to oxidize significant quantities of reduced nitrogen forms in the 5-day BOD test. Currently any biological treatment plant effluents contain a significant population of nitrifying organisms. Consequently, oxidation of nitrogenous compounds can occur within such samples and inhibition of nitrification is recommended for all samples of secondary effluent, for samples seeded with secondary effluent, and for samples of polluted waters.

Samples for BOD analysis may undergo significant degradation during storage between collection and analysis. This results in a low BOD value. Minimize reduction of BOD by promptly analyzing the sample or by cooling it to near-freezing temperature during storage. However, even at low temperature, holding time should be limited to a minimum.

If analysis is initiated within 2 hr of collection sample cooling is unnecessary. If analysis of a grab sample is not started within 2 hr of collection, keep sample at or below 4 C from time of collection; if the laboratory is on the site or in the vicinity of the sample collection site, begin analysis within 6 hr of collection; if the laboratory is more remote begin analysis within 24 hr of collection.

Keep composite samples at or below 4 C during compositing and any holding period; limit the compositing period to 24 hr; if the laboratory is on site or nearby, begin analysis not more than 6 hr after the end of the compositing period; if the laboratory is distant, begin incubation not more than 24 hr after the end of the compositing period.

The method outlined here contains both a dilution water check (4*i*), and a dilution water blank (4*g*). In the dilution water check, the candidate dilution water is lightly seeded. An oxygen up take in 5 days of less than 0.2 mg/L is acceptable. If the oxygen depletion of a candidate water exceeds this value store the water at room temperature (or 20 C) until the BOD of the dilution water is reduced sufficiently. Optimally, test and store dilution water so that water of assured quality always is on hand.

The procedure for determining immediate oxygen demand (IDOD) has been eliminated because: (1) It was not clear whether IDOD should be reposted in 5-day BOD data; (2) the measurement was inaccurate because of the small differences between initial DO and DO after 15 min; (3) arbitrary selection of 15 min for measuring IDOD did not necessarily include all short term oxygen-consuming chemical oxidations; and (4) the IDOD is in some cases, an iodine demand (during the DO determination) rather than true DO demand. The methods outlined here require determining initial DO 15 min after making the dilution.

Although only the 5-day BOD is described here, many variations of oxygen demand measurements exist. These include using shorter and longer incubation periods, tests to determine rates of oxygen use, continuous oxygen measurements by respirometric technique, etc.

2. Apparatus

a. Incubation bottles, 250 to 300 mL capacity, with ground-glass stoppers. Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use *a* water seal. Obtain satisfactory water seals by inverting the bottles in a water bath or adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over the flared mouth of the bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at 20±1 C. Exclude all light to prevent formation of DO by algae in the sample.

3. Reagents

a. Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7H_2O$, and 1.7 g NH_4Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without further adjustment. Discard reagent (or any of the following reagents) if there is any sign of biological growth in the stock bottle.

b. Magnesium sulfate solution: Dissolve 22.5 g $M_gSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.

c. Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

d. Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L.

e. Acid and alkali solutions, 1N: for neutralization of caustic or acidic waste samples.

f. Sodium sulfite solution, 0.025*N:* Dissolve 1.575 g Na_2SO_3 in 1,000 mL distilled water. This solution is not stable; prepare daily.

g. Nitrification inhibitor: Reagent grade 2-chloro-6 (trichloro methyl) pyridine.[1]

4. Procedure

a. Preparation of dilution water: Use water for diluting samples that meets the dilution water check (4*i*) and the glucose-glutamic acid check (4*j*). If necessary purify by storing long enough to degrade organic contaminants or by other methods. If storage for biological degradation is used, seed the water as described in the dilution water check (4*h*) before storage. Store dilution water in the dark or cover it to exclude light to control algal growth. Use dilution water at 20±1 C. Protect water quality by using clean glassware, tubing, and bottles.

Before use, saturate the water with DO by shaking it in a partially-filled bottle or by aerating with filtered air. Alternatively, store in cotton-plugged bottles long enough for the water to become saturated with DO.

Place the desired volume of distilled water in a suitable bottle and add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water.

b. Seeding: A population of microorganisms capable of oxidizing the sample biodegradable organic matter is necessary. Domestic wastewater, unchlorinated, or otherwise-undisinfected effluents of biological treatment plants, and surface waters contain satisfactory microbial populations. When the sample is unlikely to contain enough desired micro-organisms, for example, in some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values, add a population of appropriate microorganisms to the dilution water. This procedure is called *seeding.* The preferred seed is effluent from a biological treatment system processing the waste. Where this is not available, use supernatant from domestic wastewater after settling at 20 C for at least 1 hr but no longer than 36 hr.

Some samples may contain materials not degraded at normal rates by a microorganism in settled domestic wastewater. Seed such samples with an adapted microbial population obtained from the undisinfected effluent of a biological treatment process receiving the waste. In the absence of such a facility, obtain seed from the receiving water below (preferably 3 to 8 km) the point of discharge. When such seed sources also are not available, develop a seed in the laboratory by continuously aerating a sample of settled domestic sewage and adding small daily increments of waste. Optionally add soil or activated sludge to obtain the initial microbial population. Determine the existence of a satisfactory population by testing the seed response in BOD tests of the sample. BOD values increasing with time of adaption to a steady high value indicate successful seed adaption.

In making tests, use enough seed to assure satisfactory numbers of microorganisms but not so mush that the oxygen demand of the seed itself is a major part of the oxygen used during incubation. The oxygen used by the seed should be at least 0.6 mg/L, but not more than 1.0 mg/L. Subtract the oxygen used by the seed material from the total oxygen used to obtain the oxygen used by the sample (see 507.5). Determine oxygen depletion of the seed by measuring its BOD as for any other sample. This is called the seed control.

The addition of seed to dilution water is described for each of the two dilution technics in #4*d.*

c. Pretreatment:

(1) Samples containing caustic alkalinity or acidity-Neutralize samples to pH 6.5 to 7.5 with H_2SO_4 or NaOH

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[1] N-Serve, Dow Chemical Co. as equivalent

solutions of such strengths that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of seeded dilution water should not be changed by preparation of the lowest dilution of sample.

(2) Samples containing residual chlorine compounds—If possible avoid samples containing residual chlorine by sampling before chlorination. If residual chlorine is present, dechlorinate and seed the sample (#4*b*). Do not test chlorinated/dechlorinated samples without seeding. In some samples chlorine will dissipate within 1 to 2 hr of standing in the light. This often occurs during sample transport and handling. For samples in which the chlorine residual does not dissipate on standing in a reasonably short time, destroy the chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100 to 1,000 mL portion of neutralized sample by adding 10 mL of 1+1 acetic acid or 1+50 H_2SO_4, 10 mL KI solution (10 g/100 mL), and titrating with 0.025*N* Na_2SO_3 solution to the starch—iodide end point. Add to sample the volume of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 min check sample for residual chlorine.

(3) Samples containing other toxic substances—Samples such as those from certain industrial wastes-for example, toxic metals derived from plating wastes—frequently require special study and treatment.

(4) Samples supersaturated with DO-Samples containing more than 9 mg DO/L at 20 C may be encountered during winter months or where algae are growing actively. To prevent loss of oxygen during incubation of these samples, reduce DO to saturation by bringing sample to about 20 C in a partly filled bottle and agitating it by vigorous shaking or by aerating with compressed air.

(5) Sample temperature adjustment—Bring samples to 20±1 C before making dilutions.

(6) Nitrification inhibition—To inhibit nitrification where sample or seed way contain sufficient nitrifying organisms to result in significant oxidation of reduced nitrogen forms and nitrogenous BOD is not desired; add 10 mg 2-chloro-6 (trichloro methyl) pyridine/L. Such samples include, but are not limited to, biologically treated effluents, samples seeded with biologically treated effluents, and river waters.

d. Dilution technic: Make several dilutions of prepared sample to obtain required DO depletions. Dilutions that result in a residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L after 5 days incubation produce the most reliable results. The sample oxygen demand governs dilution needed. Experience with a particular sample will permit using a smaller number of dilutions. A more rapid analysis, such as COD may be correlated approximately with BOD and serve to guide dilution. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled sewage, 5 to 25% for oxidized effluent, and 25 to 100% for polluted river waters. Prepare dilutions either in graduated cylinders and then transfer to BOD bottles or prepare dirtectly in BOD bottles. Either method of preparation can be combined with any of the DO measurement technics. The number of bottles to be prepared depends on the method of determining DO and the number of replicates desired.

(1) Dilutions prepared in graduated cylinders—

If the azide modification of the iodometric method (titration) see section (421B) is used, carefully siphon dilution water, seeded if necessary, into a graduated cylinder of 1,000 to 2,000 mL capacity, filling the cylinder half full without entrainment of air. Add quantity of carefully mixed sample to make desired dilution and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod, avoiding entrainment of air. Siphon mixed dilution into two BOD bottles, one for incubation and the other for determining initial DO in the mixture; stopper tightly and incubate for 5 days at 20 C.

If the membrane electrode method is used, siphon dilution mixture into only one BOD bottle.

Prepare succeeding dilutions of lower concentration in the same manner or add dilution water to unused portion of preceding dilution. If seeding is necessary, either add seed directly to dilution water or to individual cylinders before dilution. Seeding individual cylinders avoids a declining ratio of seed to sample as increasing dilutions are made.

(2) Dilutions prepared directly in BOD bottles—

Pipet required volume of sample, using a wide-tip volumetric pipet, into individual BOD bottles of known capacity. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubble. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle.

e. Determination of initial DO: Determine initial DO 15 min after preparing dilution if materials are present in the sample that react rapidly with DO. If the oxygen used by such materials is insignificant, the time period between preparing dilution and measuring initial DO is not critical.

Use the azide modification of the iodometric method (see section 421B) or the membrane electrode method (see section 421F) to determine initial DO on bottles containing all sample dilutions, dilution water blanks, and where appropriate, seed controls.

For activated sludge samples use either the membrane electrode method or the $CuSO_4$-sulfamic acid modification of the iodometric method (see section 421E). For muds use either the membrane electrode method or the alum-flocculation modification of the iodometric method (see section 421D). If the membrane electrode is used to determine initial and final DO values on the same bottle, replace with dilution water any small volume of bottle contents lost by overflowing when membrane electrode is inserted. Alternatively add a small marble or glass beads to the bottle so that water in the bottle is raised to such a level that the stopper can be inserted without entrapping any air bubbles.

f. Incubation: Incubate prepared BOD bottles of samples and dilution water for 5 days in the dark at 20 ± 1 C. Make a water-seal on BOD bottles by inverting them in a tray of water in the incubator or by using a special water-seal bottle.

g. Dilution water blank: For each batch of samples and for each container of dilution water fill 2 BOD bottles with unseeded dilution water. Use dilution water which has been found satisfactory by the dilution water check (#4*i*) and the glucose-glutamic acid check (4*j*). Stopper water-seal, incubate, and after 5 days, measure DO in one of these. Determine DO before incubation in the other bottle. Use these DO results as a rough check on the quality of dilution water and cleanliness of incubation bottles. The difference in DO should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.

h. Determination of final DO: After incubation determine DO in incubated samples and blank as in #4*e* above.

i. Dilution water check: Seed dilution water with a quantity of seed sufficient to cause an oxygen use of 0.05 to 0.1 mg/L during the 5-day incubation. If dilution water has been seeded and stored for degradation, omit seeding specified above in any subsequent dilution water check. Fill two BOD bottles, stoppers, water-seal and determine DO immediately in one of these. Incubate the second bottle at 20 C for 5 days and then determine DO. Use DO results on these two bottles as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. The difference in DO should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L. If more DO is consumed, reject results obtained using this dilution water.

j. Glucose-glutomic acid check: The BOD test is a bioassay procedure; consequently, results are influenced greatly by toxic substances or use of a poor seeding material. Even distilled waters frequently are contaminated with toxic substances—most often copper—and some sewage seeds are relatively inactive. The results obtained using such waters are always low. Check quality of dilution water effectiveness of seed, and analytical technic periodically by using pure organic compounds. Alternatively, if a known organic compound is a major component of a particular waste it may be used in place of glucose-glutamic acid for this check. For general BOD work on samples not requiring an adapted seed, use a mixture of glucose and glutamic acid containing 150 mg of each/L. Glucose has an exceptionally high and variable oxidation rate but when used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes.

Prepare a solution containing 150 mg/L each of reagent-grade glucose and glutamic acid that have been dried at 103 C for 1 hr. Determine the BOD of this mixture using a 2% dilution in the incubation bottles and seeding according to #4*b*. Make a dilution water check, #4*i*, and a seed control determination, #4*b*. The glucose-glutamic acid solution is subject to biological degradation and should not be stored more than a few hr.

The precision and accuracy of the test is discussed in P 6 below. If the BOD value of the check is outside the range of 200 ± 37 mg/L, reject any BOD value obtained using the seed and dilution water and seek cause of problem.

5. Calculation

a. Definitions

D_1 = DO of diluted sample 15 min after preparation, mg/L

D_2 = DO of diluted sample after incubation, mg/L

P = decimal fraction of sample used

B_1 = DO of dilution of seed control before incubation, mg/L

B_2 = DO of dilution of seed control after incubation, mg/L

f = ratio of seed in sample to seed in control

$$= \frac{\%\ \text{seed in } D_1}{\%\ \text{seed in } B_1}$$

b. Biochemical oxygen demand

When sample dilution is not seeded

$$\text{BOD mg/L} = \frac{D_1 - D_2}{P}$$

When sample dilution is seeded

$$\text{BOD mg/L} = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

If more than one dilution of a sample meets the criterion of a residual DO of at least 2 mg/L and there is no evidence of a toxic effect at the higher concentration or an obvious anomaly, average results.

In these calculations, corrections are not made for use of DO in the dilution water blank during incubation. If the dilution water does not meet the dilution water blank criteria, proper corrections are difficult and results are questionable.

6. Precision and Accuracy

In a series of interlaboratory studies, each involving 86 to 102 laboratories (and as many river water and sewage seeds), 5-day BOD analyses were performed on synthetic water samples containing 50/50 mixtures of glucose and glutamic acid in the range of 5 to 340 mg/L. The regression equations for mean value X, *and standard deviation*, S, from these studies were as follows:

X=0.665 (added level, mg/L) −0.149

S=0.120 (added level, mg/L) + 1.04

At the 300 mg/L level of the mixed primary standard, the average 5-day BOD was 199.4 mg/L with a standard deviation of 37.0 mg/L2.

7. References

1. *Young, J. C.* 1979. Chemical methods for nitrification control *J. Water Pollute Control Fed.* 45:637.

2. United States Environmental Protection Agency, Office of Research & Development, Environmental Monitoring & Support Laboratory, Cincinnati, Ohio.

In consideration of the preceding, it is proposed to amend chapter I, Subchapter D of Title 40, Code of Federal Regulations, as follows:

§ 136.3 [Amended]

1. Table I of § 136.3(a) is amended by:

(a) Addition of a new subsection entitled "Organic Compounds" which includes 114 specific organic parameters and approved methods by which they are to be analyzed,

(b) By redesignating parameter #9 (Benzidine) and #95 (Pentachlorophenol) as organic compounds and including them in proper alphabetical order within the organic compound subsection,

(c) By including the pesticides Aldrin, d-BHC, g-BHC, Chlordane, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, Dieldrin, Endosulfan, Endrin, Heptachlor as specific organic compounds and retaining all other pesticides within the general parametric designation, "Pesticides", and revising footnote 12,

(d) By addition of the Inductively Coupled Plasma Optical Emission Spectrometric Method (ICP) as an approved alternate method for the following metals Aluminum, Arsenic, Barium, Beryllium, Boron, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Potassium, Selenium, Silica, Silver, Sodium, Vanadium and Zinc,

(e) By addition of a new parameter entitled BOD 5 Carbonaceous, and,

(f) By deleting footnote 1 due to new table II prescribing mandatory preservation techniques and maximum holding times, and,

(g) By changing the chronological numbering of parameters and footnotes to accommodate the new parameters to read as follows:

* * * * *

Table 1.—*List of Approved Test Procedures*

Parameter and units	Method	Reference (Page Nos.)				
		1974 EPA Methods	14th edition standard methods	Part 31 1975 ASTM	USGS methods [1]	Other approved methods
1. Acidity, as $CaCO_3$, milligrams per liter	Electrometric end point (pH of 8.2) or phenolphathalein end point.	1	273(4d)	116	40	[9](607)
2. Alkanlinity, as $CaCO_3$ milligrams per liter	Electrometric titration (only to pH 4.5) manual or automated, or equivalent atomoated methods.	3 5	278	111	41	[9](607)
3. Ammonia (as N), milligrams per liter	Manual distillation [3] (at pH 9.5) followed by nesslerization, titration, electrode, automated phenolate.	159 165 168	410 412 616	237	116	[9](614)
Bacteria						
4. Coliform (fecal) [4] number per 100 ml	MPN; [5] membrane filter		922 937		[9](45)	[4,9](132) [4,9](124)
5. Coliform (fecal) [4] in presence of chlorine, number per 100 ml.	MPN; [5] membrane filter [5, 7]		922 928, 937			
6. Coliform (total), [4] number per 100 ml	MPN; [5] membrane filter		916 928		[9](35)	[4,9](117)
7. Coliform (total) [4] in presence of chlorine, number per 100 ml.	MPN; [5] membrane filter with enrichment		916 933			[4,9](108)
8. Fecal streptococci, [4] number per 100 ml	MPN; [5] membrane filter; plate count		943 944 947		[9](50)	[4,9](136) [4,9](143)
9. Biochemical oxygen demand, 5-day (BOD_5) milligrams per liter.	Winkler (Azide Modification) or electrode method.		543		[9](50)	[9](17)
10. BOD_5 Carbonaceous						[29](507)
11. Bromide, milligrams per liter	Titrimetric, iodine-iodate	14		323	58	
12. Chemical oxygen demand (COD), milligrams per liter.	Dichromate reflux	20	550	472	125	[9](610) [9](17)
13. Chloride, milligrams per liter	Silver nitrate		303	267		
	Mercuric nitrate; or	29	304	265		[2](615)
	Automated colorimetric-ferricyanide	31	613		[10](46)	
14. Chlorinated organic compounds (except pesticides), milligrams per liter.	Gas chromatography [11]					
15. Chlorine-total residual, milligrams per liter.	Iodometric titration amperometric or		318			
	Starch-iodine end-point	35	322	278		
	DPD colorimetric or		332			
	Titrimetric methods (These last two are interim methods pending laboratory testing.).		329			
16. Color, platinum cobalt units or dominant wave length, hue, luminance, purity.	Colorimetric	36	64		82	
	Spectrophotometric; or	39	66			
	ADMI procedure [12]					
17 Cyanide, total [13] milligrams per liter	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric.	40	361	503	85	[9](22)
18. Cyanide amenable to chlorination, milligrams per liter.	Distillation followed by silver nitrate titration or pyridine pyrazolone (or barbituric acid) colorimetric.	49	376	503		
19. Dissolved oxygen, milligrams per liter	Winkler (Azide modification) or electrode method.	51 56	553 450	368	126	[9](609)
20. Fluoride, milligrams per liter	Distillation [3] followed by	65	389	307	93	
	ion electrode	59	391	305		
	SPADNS; or	61	393			
	automated complexane		614			
21. Hardness—total, as $CaCo_3$, milligrams per liter.	EDTA titration	68	202	161	94	[9](617)
	Automated colorimetric; or atomic absorption (sum of Ca and Mg as their respective carbonates).	70				
22. Hydrogen ion (pH), pH units	Electrometric measurement	239	460	178	129	[9](606)
23. Kjeldahl nitrogen (as N), milligrams per liter.	Digestion an distillation followed by nesslerization, titration, or electrode; automated digestion automated phenolate.	175 165 182	437		122	[9](612)
METALS						
24. Aluminum—total, milligrams per liter	Digestion [14] followed by atomic absorption [15] or by colorimetric (Eriochrome Cyanide R) or by ICP [27].	92	152 171		[9](19)	
25. Aluminum—dissolved, milligrams per liter	0.45 mcron filtratoifollowed by referenced methods for total aluminum					
26. Antimony—total, milligrams per liter	Digestion [4] followed by atomic absorption [16]					
27. Antimony—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total antimony.					
28. Arsenic—total, milligrams per liter	Digestion followed by silver diethyldithiciocarbamate; or atomic absorption [15, 17] or by ICP [27].	9 95	285 283 159		[illegible] [illegible]	
29. Arsenic—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total arsenic.					
30. Barium—total, milligrams per liter	Digestion [14] followed by atomic absorption [15] or by ICP [27].					

Table 1.—*List of Approved Test Procedures* —Continued

Parameter and units	Method	Reference (Page Nos.)				
		1974 EPA Methods	14th edition standard methods	Part 31 1975 ASTM	USGS methods [1]	Other approved methods
31. Barium—dissolved, milligrams per liter	0.45 micron filtration[16] followed by referenced method for total barium.					
32. Beryllium]total, milligrams per liter	Digestion[14] followed by atomic absorption[15] or by colorimetric (Aluminan) or by ICP[27].	99	152 177			
33. Berylium—dissolved, miligram per liter	0.45 micron filtration [16] followed by referenced method for total beryllium.					
34. Boron—total, milligrams per liter	Colorimetric (Curcumin), or by ICP [27]	13	287			
35. Boron—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total boron.					
36. Cadmium—total milligrams per liter	Digestion [14] followed by atomic absorption [15] or by colorimetric (Dithizone) or by ICP [27].	101	148 182	345	62	(619) [2] (37) [9]
37. Cadmium—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total cadmium.					
38. Calcium—total, milligrams per liter	Digestion [14] followed by atomic absorption; or EDTA titration or by ICP [27].	103	148 189	345	66	
39. Calcium—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total calcium.		9			
40. Chromium VI, milligrams per liter	Extraction and atomic absorption; colorimetric (Diphenylcarbazide).	89 105	192		76 75	
41. Chromium VI—dissolved, milligram per liter.	0.45 micron filtration [16] followed by referenced method for chromium VI.					
42. Chromium—total, milligrams per liter	Digestion [14] followed by atomic absorption [15] or by colorimetric (Diphenylcarbazide) or by ICP [27].	105	148 192	345 286	78 77	(619) [2]
43. Chromium—dissolved, milligrams per liter.	0.45 micron filtration [16] followed by referenced method for total chromium.					
44. Cobalt—total, milligrams per liter	Digestion [14] followed by atomic absorption [15] or by ICP [27].	107	148	345	80	(37) [9]
45. Cobalt—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total cobalt.					
46. Copper—total, milligrams per liter	Digestion [14] followed by atomic aborption [15] or by colorimetric (Neocuproine) or by ICP [27].	108	148 196	345 293	83	(619) [2] (37) [9]
47. Copper—dissolved	0.45 micron filtration [16] followed by referenced method for total copper.					
48. Gold—total, milligrams per liter	Digestion [14] followed by atomic absorption [18]					
49. Iridium—total, milligrams per liter	Digestion [14] followed by atomic absorption [18]					
50. Iron—total, milligrams per liter	Digestion [14] followed by atomic aborption [15] or by colorimetric (Phenanthroline) or by ICP [27].	110	148 208	345 326	102	[2](619)
51. Iron—dissolved, milligrams per liter	0.45 micron filtration[16] followed by referenced method for total iron.					
52. Lead—total, milligrams per liter	digestion[14] followed by atomic absorption[15] or by colorimetric (Dithizone) or by ICP[27].	112	148 215	345	105	[2](619)
53. Lead—dissolved, milligrams per liter	0.45 micron filtration[16] followed by referenced method for total lead.					
54. Magnesium—total, milligrams per liter	Digestion[14] followed by atomic absorption; or gravimetic or by ICP[27].	114	148 221	345	109	[2](619)
55. Magnesium-dissolved, milligrams per liter.	0.45 micron filtration[16] followed by referenced method for total magnesium.					
56. Manganese—total, milligrams per liter	Digestion[14] followed by atomic absorption[15] or by colorimetric (persulfate or periodate) or by ICP[27].	116	148 225 227	345	111	[2](619)
57. Manganese—dissolved, milligrams per liter.	0.45 micron filtration[16] followed by referenced method for total manganese.					
58. Mercury—total, milligrams per liter	Flameless atomic absorption	118	156	338	[10](51)	
59. Mercury—dissolved, milligrams per liter	0.45 micron filtration[16] followed by referenced method for total mercury.					
60. Molybdenum—total milligrams per liter	Digestion[14] followed by atomic absorption[15] or by ICP[27].	139		350		
61. Molybdenum—dissolved, milligrams per liter.	0.45 micron filtration[16] followed by referenced method for total molybdenum.					
62. Nickel—total milligrams per liter	Digestion[14] followed by atomic absorption[15] or by colorimetric (Heptoxime) or by ICP[27].	141	148 232	345	115	
63. Nickel—dissolved, milligrams per liter	0.45 micron filtration[16] followed by referenced method for total nickel.					
64. Osmium—total milligrams per liter	Digestion[14] followed by atomic absorption[18]					
65. Palladium—total, milligrams per liter	Digestion[14] followed by atomic absorption[18]					
66. Platinum—total, milligrams per liter	Digestion[14] followed by atomic absorption[19]					
67. Potassium—total, milligrams per liter	Digestion[14] followed by atomic absorption, colorimetric (Cobaltinitrite), or by flame photometric or by ICP[27].	143	235 234	403	134	[2](620)
68. Potassium—dissolved, milligrams per liter.	0.45 micron filtration[16] followed by referenced method for total potassium.					
69. Rhodium—total, milligrams per liter	Digestion[14] followed by atomic absroption[18]					
70. Ruthenium—total, milligrams per liter	Digestion[14] followed by atomic absorption[18]					
71. Selenium—total, miligrams per liter	Digestion[14] followed by atomic absorption[17, 15] or by ICP[27].	145	159			
72. Selenium—dissolved, milligrams per liter	0.45 micron filtration[16] followed by reference method for total selenium.					
73. Silica—dissolved, miligrams per liter	0.45 micron filtration[16] followed by colorimetric (Molybdosilicate) or by ICP[27].	274	487	398	139	
74. Silver-total [19], milligrams pr liter	Digestion[14] followed by atomic absorption [15] or by colorimetric (Dithizone) or by ICP[27].	146	148		142	(619)[2] (37)[9]
75. Silver-dissolved [19], milligrams per liter	0.45 micron filtration [16] followed by referenced method for total silver.					
76. Sodium—total, milligrams per liter	Digestion[14] followed by atomic absorption or by flame photometric or by ICP[27].	147	250	403	143	(621)[2]
77. Sodium—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total sodium.					

Table 1.—*List of Approved Test Procedures* —Continued

Parameter and units	Method	Reference (Page Nos.)				
		1974 EPA Methods	14th edition standard methods	Part 31 1975 ASTM	USGS methods [1]	Other approved methods
78. Thallium—total, milligrams per liter	Digestion [14] followed by atomic absorption [15]	149				
79. Thallium—dissolved, milligrams per liter	0.45 micron filtration [16] followed by referenced method for total thallium.					
80. Tin—dissolved, milligrams per liter	filtration [14] followed by atomic absorption [15]	150			[19](65)	
81. Tin—dissolved, milligrams per liter	0.45 filtration [16] followed by referenced method for total tin.					
82. Titanium—total, milligrams per liter	Digestion [14] followed by atomic absorption [15]	151				
83. Titanium—dissolved, milligrams per liter	0.45 filtration [16] followed by referenced method for total titanium.					
84. Vanadium—dissolved, milligrams per liter	Digestion [14] followed by atomic absorption [15] or by colorimetric (Gallic acid) or by ICP [27].	153	152 260	441	[19](67)	
85. Vanadium—dissolved milligrams per liter	0.45 micron filtration [16] followed by referenced method for total vanadium.					
86. Zinc—total, milligrams per liter	Digestion [14] followed by atmoic absorption [15] or by colorimetric (Dithizone) or by ICP [17].	155	148 265	345	159	[2] (619) [8] (37)
87. Zince—dissolved, milligrams per liter	0.45 micro filtration [16] followed by referenced method for total zinc.					
88. Nitrate (as N), milligrams per liter	Cadmium reduction brucine sulfate; automated cadmium or hydrazine reduction [20].	201 197 207	423 427 620	358	119	[2] (614) [8] (28)
89. Nitrate (as N), milligrams per liter	Manual or automated colorimetric (Diazotization)..	215	434		121	
90. Oil and grease, milligrams per liter	Liquid-liquid extraction with trichlorotrifluoroethane-gravimetric.	229	515			
91. Organic carton; total (TOC), milligrams per liter.	Combustion—infrared method [2]	236	532	467	[22] (4)	
92. Organic nitrogen (as N), milligrams per liter.	Kjeldahl nitrogen minus ammonia nitrogen	175,159	437		122	[2] (612,614)
ORGANIC COMPOUNDS						
93. Acenaphthene, micrograms per liter	GC or HPLC method (610) [35]; GC/MS method (625) [36].					
94. Ancenaphthylene micrograms per liter	GC or HPLC method (610) [35]; GC/MS method (625) [36].					
95. Acrolein, micrograms per liter	GC or HPLC method (603) [31]; GC/MS method (624) [36].					
96. Acrylonitrile, micrograms per liter	GC or HPLC method (603) [31]; GC/MS method (624) [26].					
97. Aldrin, micrograms per liter	GC or HPLC method (608) [34]; GC/MS method (625) [26].					
98. Anthracene, micrograms per liter	GC or HPLC method (610) [35]; GC/MS method (625) [36].					
99. Benzene, micrograms per liter	GC or HPLC method (602) [30]; GC/MS method (624) [36].					
100. Benzidine milligrams per liter, micrograms per liter.	HPLC method (605) [33]; Oxidation-colormetric [5]; GC/MS method (625) [26].					
101. Benzo(a)anthracene, micrograms per liter.	GC or HPLC method (610) [34]; GC/MS method (625) [20].					
102. Benzo(a)pyrene, micrograms per liter	GC or HPLC method (610) [34]; GC/MS method (625) [26].					
103. Benzo(b)fluroanthene, micrograms per liter.	GC or HPLC method (610) [36]; GC/MS method (625) [36].					
104. Benzo(g,h,i)perylene, micrograms per liter.	GC or HPLC method (610) [35]; GC/MS method (625) [36].					
105. Benzo (k) fluoranthene, micrograms per liter.	GC or HPLC method (610) [34]; GC/MS method, (625) [28].					
106. a-BHC, microgram per liter	GC method (608) [38]					
107. b-BHC, micrograms per liter	GC method (608) [36]; GC/MS method (625) [28]					
108. d-BHC, microgram per liter	GC method (608) [26]; GC/MS method (625) [28]					
109. g-BHC; micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
110. Bis(2-chloroethyl) either, micrograms per liter.	GC method (611) [38]; GC/MS method (625) [26]					
111. Bis(2-chloroethoxy) methane, micrograms per liter.	GC method (611) [38]; GC/MS method (625) [26]					
112. Bis(2-chloroisopropyl) ether, micrograms per liter.	GC method (611) [38]; GC/MS method (625) [28]					
113. Bis(2-ethylhexyl)phthalate, micrograms per liter.	GC method (606) [34]; GC/MS method (625) [36]					
114. Bromodichloromethane, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [36]					
115. Bromoform, micrograms per liter	GC method (601) [29]					
116. Bromomethane, micrograms per liter	GC method (601) [29]; GC/MS method (624) [26]					
117. 4-Bromophenylphenyl ether, micrograms per liter, cicrograms per liter.	GC method (611) [30]; GC/MS method (625) [26]					
118. Burylbenzyul phthalate, micrograms per liter.	GC method (606) [34]; GC/MS method (625) [24]					
119. Carbon tetrachloride, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [38]					
120. Chlordane, micrograms per liter	GC method (608) [34]; GC/MS method (625) [26]					
121. 4-Chloro-3-methylphenol, micrograms per liter.	GC method (604) [33]; GC/MS method (625) [38]					
122. Chlorobenzene, micrograms per liter	GC methods (601) [29] (602) [30]; GC/MS, method (624) [26].					
123. Chloroethane, micrograms per liter	GC method (601) [29]; GC/MS, method (624) [26]					
124. 2-Chloroethylvinyl either, micrograms per liter.	GC method (601) [26]; GC/MS, method (624) [26]					
125. Chloroform, micrograms per liter	GC method (601) [29]; GC/MS, method (624)26					

Table 1.—*List of Approved Test Procedures*—Continued

Parameter and units	Method	Reference (Page Nos.)				
		1974 EPA Methods	14th edition standard methods	Part 31 1975 ASTM	USGS methods [1]	Other approved methods
126. Chloromethane, micrograms per liter	GC method (601)[26]; GC/MS method (624)[38]					
127. Chloronmethane, micrograms per liter	GC method (612)[40]; GC/MS method (625)[38]					
128. 1–Chlorophenol, microgram per liter	GC method (604)[33]; GC/MS, method (625)[38]					
129. 4-Chlorophenylphenyl ether, micrograms per liter.	GC method (611)[39]; GC/MS, method (625)[35]					
130. Chrysene, micrograms per liter	GC or HPLC method (610)[34]; GC/MS method (625)[39].					
131. 4,4'-DDD, micrograms per liter	GC method (608)[36]; GC/MS method (625)[39]					
132. 4,4'-DDE, micrograms per liter	GC method (608)[36]; GC/MS method (626)[39]					
133. 4,4'-DDT, micrograms per liter	GC method (608)[35]; GC/MS method (625)[39]					
134. Dibenzo(a,h) anthracene, micrograms per liter.	GC or HPIC method (610)[38]; GC/MS method (625)[38].					
135. Dibromochloramethane, micrograms per liter.	GC method (610)[29]; GC/MS method (624)[38]					
136. 1,2-Dichlorobenzene, micrograms per liter.	GC metdhods (601)[29] (602)[30] (612)[40]; GC/MS method (626)[26].					
137. 1,3-Dichlorobenzene, micrograms per liter.	GC methods (601)[33] (602)[30] (612)[40]; GC/MS method (625)[26].					
138. 2,4-Dichlorobenzene, micrograms per liter.	GC methods (601)[29] (602)[30] (612)[40]; GC/MS method (625)[26].					
139. 3,3'-Dichlorobenzidine, micrograms per liter.	HPIC method (605)[33]; GC/MS method (625)[35]					
140. Dichlorodifluoromethane, micrograms per liter.	GC method (601)[29]					
141. 1,1-Dichloroethane, micrograms per liter.	GC method (601 [29]; GC/MS method (624)[38]					
142. 1,2-Dichlorethane, micrograms per liter	GC method (601)[29]; GC/MS method (624)[39]					
143. 1,2-Dichloromethane, micrograms per liter.	GC method (601)[29]; GC/MS method (624)[39]					
144. trans-1,2-Dichloromethane, micrograms per liter.	GC method (601)[29]; GC/MS method (624)[36]					
145. 2,4-Dichlorophenol, micrograms per liter.	GC method (604)[33]; GC/MS method (625)[39]					
146. 1,2-Dichlorpropane, micrograms per liter.	GC method (601)[29]; GC/MS method (624)[38]					
147. cis-1,3-Dichloropropene, micrograms per liter.	GCC method (601) 29; GC/MS method (624)[35]					
148. trans-1,3-Dichlorpropene, micrograms per liter.	GC method (601)[29]; GC/MS method (624)[35]					
149. Dieldrin, micrograms per liter	GC method (608)[36]; GC/MS method (625)[35]					
150. Diethyl phthalate, micrograms per liter	GCC method (606)[34]; GC/MS method (625)[39]					
151. 2,4-Dimethylphenol, micrograms per liter	GC method (604)[33]; GC/MS method (625)[39]					
152. Dimethyl phthalamate, micrograms per liter.	GC method (606)[34]; GC/MS method (625)[36]					
153. Di-n-butyl phthalate,	GC method (606)[34]; GC/MS method (625)[35]					
154. Di-n-octyl phthalate, micrograms per liter	GC method (606)[34]; GC/MS method (625)[36]					
155. 4,6-Dinitro-2-methylphenol, micrograms per liter.	GC method (604)[33]; GC/MS method (625)[38]					
156. 2,4-Dinitrophenol, micrograms per liter	GC method (604)[35]; GC/MS method (625)[36]					
157. 2,4-Dinitrotoluene, micrograns per liter	GC method (609)[37]; GC/MS method (625)[36]					
158. 2,6-Dinitrotoluene, micrograms per liter	GC method (609)[37]; GC/MS method (625)[36]					
159. 1,2-Diphenylhydrazine, micrograms per liter.	GC/MS method (625)[36]					
160. Endosulfan I, micrograms per liter	GC method (608)[36]; GC/MS method (625)[36]					
161. Endosulfan II, micrograms per liter	GC method (608)[38]; GC/MS method (625)[39]					
162. Endosolfan sulfate, micrograms per liter.	GC method (608)[36]; GC/MS method (625)[35]					
163. Endrin, micrograms per liter	GC method (608)[36]; GC/MS method (625)[36]					
164. Endrin aldehyde, micrograms per liter	GC method (608)[36]; GC/MS method (625)[36]					
165. Ethylbenzene, micrograms per liter	GC method (602)[30]; GC/MS method (624)[35]					
166. Fluoranthene, micrograms per liter	GC or HPLC method (610)[35]; GC/MS method (625)[36].					
167. Fluorene, micrograms per liter	GC or HPLC method (610)[35]; GC/MS method (625)[36].					
168. Heptachlor, micrograms per liter	GC method (608)[36]; GC/MS method (625)[38]					
169. Heptachlor epoxide, micrograms per liter	GC method (608)[36]; GC/MS method (625)[36]					
170. Hexachlorobenzene, micrograms per liter.	GC method (612)[40]; GC/MS method (625)[39]					
171. Hexachlorobutadiene, micrograms per liter.	Gc method (612)[40]; GC/MS method (625)[38]					
172. Hexachlorocyclopentadiene, micrograms per liter.	GC method (612)[40]; GC/MS method (625)[39]					
173. Hexachloroethane, micrograms per liter	GC method (612)[40]; GC/MS method (625)[39]					
174. Indeno (a,3,3-od) pyrene, micrograms per liter.	GC or HPLC method (610)[35]; GC/MS method (625)[36].					
175. Isophorone, micrograms per liter	GC method (609)[37]; GC/MS method (625)[38]					
176. Methylene chloride, Micrograms per liter.	GC method (601)[29]; GC/MS method (624)[28]					
177. Naphthalene, micrograms per liter	GC or HPLC method (610)[35]; GC/MS method (625)[36].					
178. Nitrobenzene, micrograms per liter	GC method (609)[37]; GC/MS method (625)[36]					
179. 2-Nitrophenol, micrograms per liter	GC method (604)[33]; GC/MS method (625)[39]					
180. 4-Nitrophenol, micrograms per liter	GC method (604)[33]; GC/MS method (625)[36]					
181. N-Nitrosodimethylamine, micrograms per liter.	GC method (607)[35]; GC/MS method (625)[39]					
182. N-Nitrosodipropylamine, micrograms per liter.	GC method (607)[35]; GC/MS method (625)[36]					
183. N-Nitrosodiphenylamine, micrograms per liter.	GC method (607)[33]; GC/MS method (625)[35]					
184. PCB-1016, micrograms per liter	GC method (608)[36]; GC/MS method (625)[36]					

Table 1.—*List of Approved Test Procedures* —Continued

Parameter and units	Method	Reference (Page Nos.) 1974 EPA Methods	14th edition standard methods	Part 31 1975 ASTM	USGS methods [1]	Other approved methods
185. PCB-1221, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
186. PCB-1232, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
187. PCB-1242, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
188. PCB-1248, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
189. PCB-1254, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
190. PCB-1260, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
191. Phenanthrene, micrograms per liter	GC method (608) [38]; GC/MS method (625) [26]					
192. Phenanthrene, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
193. Phenol, micrograms per liter	GC method (604) [33]; GC/MS method (625) [26]					
194. Pyrene, micrograms per liter	GC ir HPLC method (610) [38]; GC/MS, method (625) [26].					
195. 2,3,7,8-Tetrachlorodibenzo-p-dioxin micrograms per liter.	GC/MS methods (613) [41], (625) [26]					
196. 1,1,2,2-Tetrachloroethane, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [26]					
197. Tetrachloroethene, micrograms per liter	GC method (601) [29]; GC/MS method (624) [26]					
198. Toluene, micrograms per liter	GC method (602) [30]; GC/MS method (624) [26]					
199. Toxaphene, micrograms per liter	GC method (608) [36]; GC/MS method (625) [26]					
200. 1,2,4-Trichlorobenzene, micrograms per liter.	GC method (612) [40]; GC/MS method (625) [26]					
201. 1,1,1-Trichloroethane, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [26]					
202. 1,1,2-Trichloroethane, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [26]					
203. Trichloroethene, micrograms per liter	GC method (601) [29]; GC/MS method (624) [26]					
204. Trichlorofluromethane, micrograms per liter.	GC method (601) [29]; GC/MS method (624) [26]					
205. 2,4,6,-Trichlorophenol, micrograms per liter.	GC method (601) [29]; GC/MS method (625) [26]					
206. Vinyl Chloride, micrograms per liter	GC method (601) [29]; GC/MS method (624) [26]					
207. Orthophosphate (as P), milligrams per liter.	Manual or automated ascorbic acid reduction	249 256	481 624	384	131	[16] (621)
208. Pesticides, milligrams per liter	Gas chromatography [19]		555	529	[11] (24)	
209. Phenols, milligram per liter	Colorimetric, (4AAP)	241	582	545		
210. Phosphorus (elemental), milligrams per liter.	Gas chromatography [23]					
211. Phosphorus; total (as P), milligrams per	Persulfate digestion followed by manual or automated ascorbic acid reduction.	249 256	476 481 624	384	133	[2] (621)
RADIOLOGICAL						
212. Alphas—total, pCi per liter	Proportional or scintillation		648	59	[16] (75) [24] (78)	
213. Alpha—counting error, pCi per liter	Proportional or scintillaiton counter		648	594	[10] (79)	
214. Beta—total, Pci per liter	Proportional counter		648	601	[16] (75) [24] (78)	
215. Beta—counting error, pCi per liter	Proportional counter		648	606	[10] (79)	
216. (a) Radium—total, pCi per liter	Proportional counter		661	661		
(b) ^{226}Ra, pCi per liter	Scintillation counter		667		[10] (81)	
RESIDUE						
217. Total, milligrams per liter	Gravimetric, 103 to 105°C	270	91			
218. Total dissolved (filterable), milligrams per liter.	Glass fiber filtration, 180°C	266	92			
219. Total suspended (non-filterable), milligrams per liter.	Glass fiber filtration, 103 to 105°C	268	94			(537) [26]
220. Settleable, milliliters per liter or milligrams per liter.	Volumetric or gravimetric		95			
221. Total volatile, milligrams per liter	Gravimetric, 550°C	272	95			
222. Specific conductuance, micromhos per centimeter at 25°C.	Wheatstone bridge conductimetry	275	71	120	148	(606) [2]
223. Sulfate (as SO_4) milligrams per liter	Gravimetric;		493	424		(624) [2]
	Turbidimetric; or	277	496	425		(623) [2]
	Automated colorimetric (barium chloranilate)	279				
224. Sulfide (as 8), milligrams per liter	Titremetric-iodine for levels greater than 1 mg per liter;.	284	505		154	
	Methylene blue photometric	—	503			
225. Sulfite (as SO_3), milligrams per liter	Titrimetric, iodine-iodate	285	508	435		
226. Surfactants, milligrams per liter	Colorimetric (Methylene blue)	157	600	494	(11) [22]	
227. Temperature, degrees C	Calibrated glass or electrometric thermometer	266	125		(131) [23]	
228. Turbidity, NIU	Nephelometric	295	132	223	156	

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[1] All page references for USGS methods unless otherwise noted are to Brown, E., Skougstad, N.W., and Fishman, M.J., "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases, "U.S. Geological Survey Techniques of Water-Resources Inv., book 5 ch. Al, (1970)."

[2] EPA comparable method may be found on indicate page of "Official Methods of Analysis of the Association of Official Analytical Chemists" methods manual, 12th ed. (1975).

[3] 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.

[4] The method used must be specified.

[5] The tube MPN is used.

[6] Slack, K.V. and others, "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples "U.S. Geological Survey Techniques of Water-Resource Inv., book 5, ch A4 (1973)."

[7] Since the membrane filter technique usually yields low and variable recovery from chlorinated wastewaters, the MPN method will be required to resolve any controversies.

[8] The chloromine-T oxidation-colometric procedure for benzedrine is available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[9] American National Standard on Photographic Processing Effluents, Apr. 2, 1975. Available from ANSI, 1430 Broadway, N.Y. 10018.

[10] Fishman, M. J. and Brown, Eugene, "Selected Methods of the U.S. Geological Survey for Analysis of Wastewaters," (1976) open-file report 76–177.

[11] Procedures for pentachlorophenol, chlorinated organic compounds, and pesticides can be obtained from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Concinnati, Ohio 45268.

[12] Color method (ADMI procedure) available from Envirnomental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[13] For samples suspected of having thiocyanate interference, magnesium chloride is used as the digestion catalyst. In the approved test procedure for cyanides, the recommended catalysts are replaced with 20 ml of a solution of 510 g/l magnesium chloride ($MgCl_2$ $6H_2O$). This substitution will eliminate thiocyanate interference for both total cyanide amenable to chloorination measurements.

[14] For the determination of total metals the sample is not filtered before processing. Because vigorous digestion procedures may result in a loss of certain metals through precipitation, a less vigorous treatment is recommended as given on p. 83 (4.1.4) of "Methods for Chemical Analysis of Water and Wastes" (1974). In those instances where a more vigorous digestion is desired the procedure on p. 82 (4.1.3) should be followed. For the measurement of the noble metal series (gold, iridium osmium, palladium, platinum, rhodium and guthenium), and aqua regia digestion is to be substituted as follows: Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of concentrated redistilled HNO_3. Place the beaker on a steam bath and evaporate to dryness. Cool the beaker and cautiously add a 5 ml portion of aqua regia. (Aqua regia is prepared immediately before use by carefully adding 3 volumes of concentrated HC1 to one volume of concentrated HNO_c.) Cover the beaker with a watch glass and return to the steam bath. Continue heating the covered beaker for 50 min. Remove cover and evaporate to dryness. Cool and take up the residue in a small, quantity of 1:1 HC1. Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to same predetermined value based on the expected metal concentration. The sample is now ready for analysis.

[15] As the various furnace devices (flameless AA) are essentially atomic absorption techniques, they are considered to be approved test methods. Methods of standard addition are to be followed as noted in p. 78 of "Methods for Chemical Analysis of Water and Wastes" 1974.

[16] Dissolved metals are defined as those constituents which pass through a 0.45 μm membrane filter. A prefiltration is permissible to free the sample from larger suspended solids. Filter the sample as soon as practical after collection using the first 50 to 100 ml to rinse the filter flask. (Glass or plastic filtering apparatus are recommended to avoid possible contamination.) Discard the portion used to rinse the flask and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH or 2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the samples.

[17] See "Atomic Absorption Newsletter," vol. 13, 75 (1974). Available from Perkin-Elmer Corp., Main Ave., Norwalk, Conn. 06852.

[18] Method available from Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[19] 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/1 20 ml of sample should be diluted to 100 ml by adding 40 each of 2M $Na_2{}^{s}{}_2O_3$ and 2M NaOH. Standards should be prepared in the same manner. For levels of silver below l mg/1 the recommended method is satisfactory.

[20] An automated hydrazine reduction method is available from the Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

[21] A number of such systems manufactured by various companies are considered to be comparable in their performance. In addition, another technique, based on combustion-methane detection is also acceptable.

[22] Goerlitz, D., Brown, E., "Methods for Analysis or Organic Substances in Water": U.S. Geological Survey Techniques of Water-Resources Inb., book 5, A3 (1972).

[23] R. F. Addison and R. G. Ackman, "Direct Determination of Elemental Phosphorous by Gas-Liquid Chromotography," "Journal of Chromatography," vol. 47, No. 3, pp. 421–426, 1970.

[24] The method found on p. 75 measures only the dissolved portion while the method on p. 78 measures only suspended. Therefore, the 2 results must be added together to obtain "total".

[25] Stevens, H. H., Fick, J. F., and Smoot, G. F., "Water Temperature—Influential Factors, Field Measurement and Data Presentation: U.S. Geological Survey Techniques of Water Resources Inv., book 1 (1975)."

[26] EPA interim methods for analysis of organics in municipal and industrial wastewater by GC/MS purge and trap (Method 624 and methylene chloride extraction (Method 625) procedures are available from the Environmental Monitoring and Support Laboratory, U.S.E.P.A., Cincinnati, Ohio, 45268. Direct Aqueous injection is to be used in these GC/MS procedures for all compounds that exceed 1000 micrograms per liter. Dichlorodifluoramethane should be analysed by the interim gas chromatographic methoc 601. For differentiation between isomeric pairs anthracene and phenanthrene, chrysene and benzo (a) anthracene, and benzo (b) fluoranthene and benzo (k) fluoranthene use method 610 polynuclear aromatic hydrocarbons. "Interim Method for Benzidine and its Salts in Wastewater" is available from the Environmental Monitoring and Support Laboratory, U.S.E.P.A., Cincinnati, Ohio, 45268 (EMSL–CI).

[27] The Inductively Coupled Plasma Optical Emission Specometric Method (ICP) is available from the Environmental Monitoring and Support Laboratory, U.SE.P.A. Cincinnati, Ohio 45268 (EMSL–CI).

[28] Method 507 for Carbonaceous Biochemical Oxygen Demand (BOD carbonaceous) is available from the Environmental Monitoring and Support Laboratory, U.S.E.P.A. Cincinnati, Ohio 45268 (EMSL–CI).

[29] Inert gas purge, followed by gas chromatography with halide specific detection (interim method 601), available from EMSL–CI.

[30] nert gas purge followed by gas chromatography and photoionization detection (interim method 602), available from EMSL–CI.

[31] Inert gas purge followed by gas chromatographic separation and detection with flame ionization detector (interim method 603), available from EMSL–CI.

[32] Methylene chloride extraction, followed by gas chromatography with flame ionization or electron capture detection (interim method 604), available from EMSL–CI.

[33] Chloroform extraction followed by concentration and high performance liquid chromatography (HPLC) with electrochemical detection (interim method 604), available from EMSL–CI.

[34] Methylene chloride extraction followed by gas chromatography with flame ionization or electron capture detection followed by gas chromatography with nitrogen-phosphorous or reductive Hall detectors (interim method 607), available from EMSL–CI.

[35] Methylene chloride extraction followed by gas chromatography with electron capture or halogen specific detection (interim method 608), available from EMSL–CI.

[37] Methylene chloride extraction followed by exchange to toluene, gas chromotography with flame ionization detection (interim method 609), available from EMSL–CI.

[38] Methylene chloride extraction followed by HPLC with fluoresence or UV detection; or gas chromatography (interim method 610), available from EMSL–CI.

[39] Methylene chloride extraction followed by gas chromatography with halogen-specific detector (inerim method 611), available from EMSL–CI.

[40] Methylene chloride extraction followed by concentration, gas chromatography with electron capture detection (interim method 612), available from EMSL–CI.

[41] Methylene chloride extraction followed by transfer to hexane and capillary column gas chromatography/mass spectometry with electron impact ionization (interim method 613), available from EMSL–CI.

[42] Microbiological Methods for Monitoring the Environment (Decembver 1978) available for the Environmental Monitoring and Support Laboratory U.S.E.P.A. Cincinnati, Ohio 45268.

2. A new § 136.3(d) is added together with a new Table entitled, "Table II—Containers, Preservation and Holding Times", to read as follows:

§ 136.3 Identification of test procedures.

* * * * * * *

(d) Sample preservation procedures, container materials, and maximum allowable holding times for parameters cited in Table I 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 in triplicate 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.—*Containers, Preservation, and Holding Times*

Measurement[a]	Container[b]	Preservative[c]	Maximum holding time[d]
1 Acidity	P,G	Cool, 4°C	14 days.
2 Alkalinity	P,G	Cool, 4°C	14 days.
3 Ammonia	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
BACTERIA			
4-7 Coliform, fecal and total	P,G	Cool, 4°C., 0.008% $Na_2S_2O_3$[h].	6 hours.
8 Fecal streptococci	P,G	Cool, 4°C., 0.008% $Na_2S_2O_3$[h].	6 hours.
9 Biochemical oxygen demand	P,G	Cool, 4°C	48 hours.
10 Biochemical oxygen demand carbonaceous.	P,G	Cool, 4°C	48 hours.
11 Bromide	P,G	None required	28 days.
12 Chemical oxygen demand	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
13 Chloride	P,G	None required	28 days
14 Chlorinated organic compounds.	G, teflon-lined cap	Cool, 4°C., 0.008% $Na_2S_2O_3$[h].	7 days (until extraction). 30 days (after extraction).
15 Chlorine, total residual	P,G	Determined on-site	2 hours.
16 Color	P,G	Cool, 4°C	48 hours.
17-18 Cyanide, total and	P,G	Cool, 4°C	14 days.
amenable to chlorination.	P,G	NaOH to pH>12 0.008% $Na_2S_2O_3$h	
19 Dissolved oxygen			
Probe	G bottle and top	Determine on site	1 hour.
Winkler	G bottle and top	Fix on site	8 hours.
20 Fluoride	P	None required	28 days.
21 Hardness	P,G	HNO_3 to pH>2	6 months.
22 Hydrogen ion (pH)	P,G	Determine on site	2 hours.
23 and 92 Kjeldahl and organic nitrogen.	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
METALS			
40-41 Chromium VI	P,G	Cool, 4°C	48 hours.
58-59 Mercury	P,G	HNO_3 to pH>2, 0.05% $K_2Cr_2O_7$.	28 days.
24-87 Metals except above	P,G	HNO_3 to pH>2	6 months.
88 Nitrate	P,G	Cool, 4°C	48 hours.
88(a)[1] Nitrate-Nitrite	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
89 Nitrite	P,G	Cool, 4°C	48 hours.
90 Oil and Grease	G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
91 Organic Carbon	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
ORGANIC COMPOUNDS[f]			
93-206 Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD).	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	7 days (until extraction). 30 days (after extraction).
Extractables (phenols)	G, teflon-lined cap	Cool, 4°C H_2SO_4 to pH>2 0.008% $Na_2S_2O_3$[h]	7 days (until extraction). 30 days (after extraction).
Purgeables (halocarbons and aromatics).	G, teflon-lined septum	Cool, 4°C., 0.008% $Na_2S_2O_3$[h].	14 days.
Purgeables (acrolein and acrylonitrite).	G, teflon-lined septum	Cool, 4°C., 0.008% $Na_2S_2O_3$[h].	3 days.
207 Orthophosphate	P,G	Filter on site, cool, 4°C	48 hours.
208 Pesticides	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	7 days (until extraction). 30 days (after extraction).
209 Phenols	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
210 Phosphorus (elemental)	G	Cool, 4°C	48 hours.
211 Phosphorus, total	P,G	Cool, 4°C., H_2SO_4 to pH>2	28 days.
RADIOLOGICAL			
212-216 Alpha, Beta and radium	P,G	HNO_3 to pH>2	6 months.
217 Residue, total	P,G	Cool, 4°C	14 days.
218 Residue, filterable	P,G	Cool, 4°C	14 days.
219 Residue, nonfilterable	P,G	Cool, 4°C	7 days.
220 Residue, settleable	P,G	Cool, 4°C	7 days.
221 Residue, volatile	P,G	Cool, 4°C	7 days.
73 Silica	P	Cool, 4°C	28 days.
222 Specific conductance	P,G	Cool, 4°C	28 days.

Table II.—*Containers, Preservation, and Holding Times—Continued*

Measurement[a]	Container[b]	Preservative[c]	Maximum holding time[d]
223 Sulfate	P,G	Cool, 4°C	28 days.
224 Sulfide	P,G	Cool, 4°C. zinc acetate	28 days.
225 Sulfite	P,G	Cool, 4°C	48 hours.
226 Surfactants	P,G	Cool, 4°C	48 hours.
227 Temperature	P,G	Determine on site	Immediately.
228 Turbidity	P,G	Cool, 4°C	48 hours.

[a] Parameter numbers refer to Table I.

[b] Polyethylene (P) or Glass (G).

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

[d] 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 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.

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 this is necessary to maintain sample stability.

[e] Samples should be filtered immediately on-site before adding preservative for dissolved metals.

[f] Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific organic compounds.

[g] This parameter not listed in Table I.

[h] Should only be used in the presence of residual chlorine.

[i] Not available in Table I.

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