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Solid Waste

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# Test Methods for Evaluating Solid Waste

## Physical/Chemical Methods

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## ABSTRACT

This manual provides test procedures which may be used to evaluate those properties of a solid waste which determine whether the waste is a hazardous waste within the definition of Section 3001 of the Resource Conservation and Recovery Act (PL 94-580). These methods are approved for obtaining data to satisfy the requirement of 40 CFR Part 261, Identification and Listing of Hazardous Waste. This manual encompasses methods for collecting representative samples of solid wastes, and for determining the reactivity, corrosivity, ignitability, and composition of the waste and the mobility of toxic species present in the waste.

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Solid Waste

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# Test Methods for Evaluating Solid Waste

## Physical/Chemical Methods

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

OFFICE OF  
SOLID WASTE AND EMERGENCY RESPONSE

Subject: Distribution of Test Methods for Solid Waste;  
Physical/ Chemical Methods (SW-846)

From: Debra Villari; Office of Solid Waste

To: Addressees

Enclosed you will find a copy of the new edition of SW-846- "Test Methods for Evaluating Solid Waste". We are able to provide a very limited number of copies to EPA personnel for their official use.

The general public can obtain this document from the Government Printing Office ( GPO Stock Number 055-002-81001-2) at a price of \$55.00. The Federal Register Notice announcing the availability of this document is attached for your referral.

If I can be of further assistance please feel free to contact me at FTS-382-4487

Boston, Massachusetts 02203, (617) 723-6486.

**SUPPLEMENTAL INFORMATION:** Part C of the Safe Drinking Water Act (SDWA) provides for an Underground Injection Control (UIC) Program. Section 1421 of the SDWA requires the Administrator to promulgate minimum requirements for effective State programs to prevent underground injection which endangers drinking water sources. The Administrator is also to list in the Federal Register each State for which in his judgment a State UIC Program may be necessary. Each State listed shall submit to the Administrator an application which contains a showing satisfactory to the Administrator that the State: (i) Has adopted after reasonable notice and public hearings, a UIC Program which meets the requirements of regulations in effect under Section 1421 of the SDWA; and (ii) will keep such records and make such reports with respect to its activities under its UIC program as the Administrator may require by regulations. After reasonable opportunity for public comment, the Administrator shall by rule approve, disapprove or approve in part and disapprove in part, the State's UIC Program.

The State of New Hampshire was listed as needing a UIC Program on March 19, 1980 (45 FR 17832). The State of New Hampshire submitted an application under Section 1422 on April 12, 1982, for the approval of an UIC Program governing Classes I, II, III, IV, and V injection wells to be administered by the New Hampshire Water Supply and Pollution Control Commission (NHWSPPCC). On May 7, 1982, EPA published notice of its receipt of the application, requested public comments, and scheduled a public hearing on the New Hampshire UIC Program submitted by the NHWSPPCC (47 FR 19726). Neither requests for public hearing nor requests to offer testimony at such hearing were received by EPA. Therefore, pursuant to the provisions of 40 CFR 123.54(c), the public hearing was cancelled on June 1, 1982 because of expressed lack of sufficient public interest.

After careful review of the application I have determined that the New Hampshire UIC Program submitted by the NHWSPPCC meets the requirements established by Federal regulations pursuant to Section 1422 of the SDWA, and hereby approve it.

#### List of Subjects in 40 CFR Part 123

Hazardous materials, Indians—lands, Reporting and recordkeeping requirements, Waste treatment and

disposal, Water pollution control, Water supply, Intergovernmental relations, Penalties, Confidential business information.

#### OMB Review

The Office of Management and Budget has exempted this rule from the requirements of Section 3 of Executive Order 12291.

#### Certification Under the Regulatory Flexibility Act

Pursuant to the provisions of 5 U.S.C. 605(b), I certify that approval by EPA under Section 1422 of the Safe Drinking Water Act of the application by the New Hampshire Water Supply and Pollution Control Commission will not have a significant economic impact on a substantial number of small entities, since this rule only approves State actions. It imposes no new requirements on small entities.

Dated: September 9, 1982.

Anne M. Gorsuch,

Administrator.

[FR Doc. 82-25942 Filed 9-20-82; 8:45 am]

BILLING CODE 6560-50-M

#### 40 CFR Parts 122 and 260

[SWH-FRL 2209-1]

#### EPA Administered Permit Programs: The Hazardous Waste Permit Program; and Hazardous Waste Management System: General

**AGENCY:** Environmental Protection Agency.

**ACTION:** Notice of availability of document; Amendment to final rule.

**SUMMARY:** The Environmental Protection Agency (EPA) is today announcing the availability of a second edition of the EPA manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846. This notice provides information on when and where the manual is available and how it differs from the first edition. This notice also amends the sections of EPA's consolidated permit regulations and hazardous waste regulations that incorporate the manual by reference, to reflect the availability of a second edition of the manual.

**EFFECTIVE DATE:** September 21, 1982.

**FOR FURTHER INFORMATION CONTACT:** The RCRA Hotline at (800) 424-9346 (toll free), or (202) 382-3000. For technical information contact David Friedman, Office of Solid Waste (WH-565), U.S. Environmental Protection Agency, 401 M

Street, S.W., Washington, D.C. 20460, (202) 755-9187.

#### SUPPLEMENTARY INFORMATION:

##### I. Second Edition of Manual

The EPA manual "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," (1980) (EPA Publication No. SW-846), is incorporated by reference in several sections of EPA's regulations. EPA first published the manual in May, 1980 when the Agency promulgated Phase I of the hazardous waste regulations in the Federal Register (45 FR 33065-33588). Three revisions to the manual—Revision A (August 1980), Revision B (July 1981), and Revision C (February 1982)—have been published since that date. EPA is today announcing the publication of a second edition of the manual which incorporates all three revisions. Although the second edition is significantly reorganized and contains additional explanatory information, EPA views this edition as equivalent to the first edition (with revisions), for regulatory compliance purposes.

##### II. Availability of Manual and Revisions

In the past, the manual and revisions to the manual have been made available to the public free of charge on request from the EPA Solid Waste Information Office in Cincinnati, Ohio. The Agency is no longer able to distribute these publications on this basis. From now on, these materials will be available to the public as follows:

● A limited number of Revisions A and B are available free of charge from the EPA RCRA Hotline (see telephone number above).

● Revision C is available for \$7.50 from the National Technical Information Service (NTIS) at 5285 Port Royal Road in Springfield, Virginia 22161. The order number is PB 82-172-158.

● The second edition of the manual is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, on a subscription basis. The subscription includes both the second edition of the manual and a number of future updates (approximately six mailings). Because the updates will be available only through this subscription, EPA recommends that persons interested in future updates to the manual subscribe to the second edition. The cost is \$55.00 per subscription for domestic mailing (\$68.75 if mailed to a foreign address).

##### III. Amendments to 40 CFR 122.20 and 260.11

Sections 122.20 and 260.11 of Title 40 of the Code of Federal Regulations set

information about publications incorporated by reference in EPA's consolidated permit regulations and hazardous waste regulations, respectively. Among other things, these comments identify the specific publications being incorporated by reference and explain how they may be obtained.

Sections 122.20 and 260.10 list the manual as one of the publications that EPA incorporates by reference in its regulations. However, they currently refer only to the 1980 edition, and indicate that the 1980 edition is available from the EPA Solid Waste Information Office in Cincinnati. As discussed above, this is no longer accurate since (1) the first edition is no longer available at all, (2) revisions to the first edition are not available from the Solid Waste Information Office, and (3) persons may use the second edition of the manual in lieu of the first edition. Accordingly, EPA is amending §§ 122.20 and 260.11 to reflect these changes.

EPA has determined under Section 553 of the Administrative Procedure Act, 5 U.S.C. 553, that there is good cause for promulgating these amendments without prior notice and opportunity for comment. These amendments are entirely technical in nature and do not change any substantive requirements. Furthermore, in light of the current inaccuracies in §§ 122.20 and 260.11, delaying promulgation of these amendments would be contrary to the public interest.

**IV. List of Subjects**

**40 CFR Part 122**

Administrative practice and procedure. Air pollution control. Hazardous materials. Reporting requirements. Waste treatment and disposal. Water pollution control. Confidential business information.

**42 CFR Part 260**

Administrative practice and procedure. Hazardous materials. Waste treatment and disposal.

Dated: September 9, 1982.

Rita M. Lavelle,  
Associate Administrator for Solid Waste and Emergency Response.

For the reasons set out in the preamble, Title 40 of the Code of Federal Regulations is amended as follows:

**PART 260—HAZARDOUS WASTE MANAGEMENT SYSTEM: GENERAL**

1. The authority citation for Part 260 reads as follows:

Authority: Secs. 1006, 2002(a), 3001-3007 and 3010 of the Solid Waste Disposal Act, as

amended (42 U.S.C. 6905, 6912(a), 6921-6927 and 6930).

2. Section 260.11 is amended by revising the fourth reference in paragraph (a) to read as follows:

**§ 260.11 References.**

(a) \* \* \*  
"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846 (First Edition, 1980, as updated by Revisions A (August, 1980), B (July, 1981), and C (February, 1982)) or (Second Edition, 1982). The first edition of SW-846 is no longer in print. Revisions A and B are available from EPA, Office of Solid Waste, (WH-565B), 401 M Street, S.W., Washington, D.C. 20460. Revision C is available from NTIS, 5285 Port Royal Road, Springfield, Virginia 22161. The second edition of SW-846 includes material from the first edition and Revisions A, B, and C in a reorganized format. It is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, (202) 783-3238, on a subscription basis, and future updates will automatically be mailed to the subscriber.  
\* \* \* \* \*

**PART 122—EPA ADMINISTERED PERMIT PROGRAMS: THE NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM; THE HAZARDOUS WASTE PERMIT PROGRAM; AND THE UNDERGROUND INJECTION CONTROL PROGRAM**

3. The authority citation for Part 122 reads as follows:

Authority: Resource Conservation and Recovery Act, 42 U.S.C. 6901 et seq.; Safe Drinking Water Act, 42 U.S.C. 300(f) et seq.; and Clean Water Act, 33 U.S.C. 1251 et seq.

4. Section 122.20 is amended by revising the first reference in paragraph (a) to read as follows:

**§ 122.20 References.**

(a) \* \* \*  
"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW-846 (First Edition, 1980, as updated by Revisions A (August, 1980), B (July, 1981), and C (February, 1982)) or (Second Edition, 1982). The first edition of SW-846 is no longer in print. Revisions A and B are available from EPA, Office of Solid Waste, (WH-565B), 401 M Street, S.W., Washington, D.C. 20460. Revision C is available from NTIS, 5285 Port Royal Road, Springfield, Virginia 22161. The second edition of SW-846 includes material from the first edition and Revisions A, B, and C in a reorganized

format. It is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, (202) 783-3238, on a subscription basis, and future updates will automatically be mailed to the subscriber.  
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[FR Doc. 82-25943 Filed 9-20-82; 8:45 am]  
BILLING CODE 6560-50-M

**DEPARTMENT OF HEALTH AND HUMAN SERVICES**

**Health Care Financing Administration  
42 CFR Part 433**

**Equipment Acquired Under Public Assistance Programs**

AGENCY: Health Care Financing Administration, HHS.  
ACTION: Final rule.

**SUMMARY:** This Final Rule revises and consolidates current regulations concerning Federal financial participation in the cost of equipment under the Medicaid Program (Title XIX of the Social Security Act). The rule also revises and consolidates current regulations on the management and disposition of equipment under the Program.

The rule would permit State public assistance agencies to claim the cost of most of their equipment at the time of purchase rather than depreciating the equipment over its useful life as required by the current regulations. This change would allow these agencies to claim Federal financial participation in the cost of the equipment at an earlier date than under the current regulations and would simplify the accounting requirements associated with the equipment.

**EFFECTIVE DATE:** October 21, 1982.

**FOR FURTHER INFORMATION CONTACT:** Edward M. Tracy, (202) 245-7411.

**SUPPLEMENTARY INFORMATION:** A Notice of proposed rulemaking was published in the Federal Register on July 24, 1981 at 46 FR 38280 inviting public comments on a proposed revision to the Departments' current regulations concerning Federal financial participation in the cost of equipment acquired under HHS supported public assistance programs. The regulation, Subpart G of 45 CFR Part 95, allows for the claiming of the cost of equipment costing \$25,000 or less in the period the equipment was acquired. Public comments were invited for 60 days ending September 22, 1981. Comments were received from eleven State or local agencies and two medical care



TEST METHODS FOR EVALUATING SOLID WASTE

—Physical/Chemical Methods—

SW-846

Second Edition

Revised

U.S. ENVIRONMENTAL PROTECTION AGENCY

APRIL 1984

U.S. Environmental Protection Agency  
Environmental Criteria System  
Office of Research and Development  
Washington, D.C. 20460  
103-20-00000-00000

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## PREFACE

This second edition of "Test Methods for Evaluating Solid Waste" contains the procedures that may be used by the regulated community or others in order to determine whether a waste is a hazardous waste as defined by regulations promulgated under Section 3001 of the Resource Conservation and Recovery Act (RCRA, PL 94-580 (40 CFR Part 261)). The manual provides methodology for collecting representative samples of the waste, and for determining the ignitability, corrosivity, reactivity, Extraction Procedure (EP) Toxicity and composition of the waste.

This document has been developed to:

- a. provide methods which will be acceptable to the Agency when used by the regulated community to support waste evaluations and listing and delisting petitions, and
- b. describe the methods that will be used by the Agency in conducting investigations under Section 3001, 3007, and 3008.

The practice of evaluating solid wastes for environmental and human health hazards is new. Experience has only recently accumulated in analyzing wastes for inorganic and organic species, and for intrinsic properties such as pH, flash point, reactivity and leachability. This manual will serve as a compilation of state-of-the-art methodology for conducting such tests. It is meant to be a dynamic document. The methodology descriptions will be frequently updated and expanded in order to keep pace with the developments being achieved by EPA, the regulated community, and others.

Standardized approved methods must be available so that the regulated community can be certain that the data it provides will be acceptable to the Agency. This manual thus makes available to the regulated community and others, those methods that the Agency considers suitable.

Many of the methods presented in this manual have not been fully evaluated by the Agency using materials characteristic of the wastes regulated under RCRA. Such evaluations are underway. However, until such time as the methods in this manual are superseded, the Agency will accept data obtained by the test methods presented in this manual. Only those data that are obtained when Quality Control and Quality Assurance procedures are followed by the testing organization will be accepted by the Agency.

This manual will eventually include a second part comprised of biological methods for determining toxic properties of RCRA wastes. Such toxic properties may include carcinogenicity, mutagenicity, teratogenicity, aquatic toxicity, phytotoxicity, and mammalian toxicity.

Methods will be provided in this present volume for the following specific areas:

- a. design of sampling and evaluation plans;

- b. collection of samples from various types of environments (e.g., pipes, drums, pits, ponds, piles, tanks);
- c. transportation and storage of samples;
- d. chain-of custody considerations to insure defensibility of data;
- e. determination of the pH, corrosivity to steel, flash point, and explosivity;
- f. conduct of the Extraction Procedure;
- g. analysis of wastes and extracts for organic and inorganic constituents;
- h. safety in solid waste sampling and testing, and
- i. quality control and quality assurance.

The analytical and sampling methods presented in this manual have been derived from a number of published sources, chiefly:

- a. "Methods for the Evaluation of Water and Wastewater," EPA-600/4-79-020, U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268,
- b. "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, September 1978,
- c. Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations; 44 FR 69464-69575, and
- d. "Samplers and Sampling Procedures for Hazardous Waste Streams," EPA-600/2-80-018, U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, OH 45268.

In addition, work conducted by and the assistance of scientists of the Environmental Monitoring Systems Laboratory at Las Vegas, NV, the Environmental Research Laboratory at Athens, GA, and the National Enforcement Investigations Center at Denver, CO, is gratefully acknowledged and appreciated.

Although a sincere effort has been made to select methods that are applicable to the widest range of expected wastes, significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Manager, Waste Analysis Program (WH-565), Waste Characterization Branch, Office of Solid Waste, Washington, D.C. 20460 (202-755-9187) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

## ACKNOWLEDGMENT

The Office of Solid Waste would like especially to thank the following individuals and groups for the help and advice they gave us during the preparation of this manual:

U.S. Environmental Protection Agency, Inductively Coupled Plasma Users Group

Dr. Theodore Martin and Dr. Gerald McKey, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio

Dr. John Warren, U.S. Environmental Protection Agency, Regulations and Standards Division, Washington, D.C.

Dr. John Maney, Dr. Curt Rose, Ann Soule, Jan Connery, Ann Gordon, Dr. Dallas Wait, Dr. Tyrone Smith, Scott Drew, and George Perry of Energy Resources Company, Inc., Cambridge, Massachusetts.

We would also like to thank the Environmental Protection Agency's Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, for providing the basic methodology used in this manual.

## SECTION ONE

### SAMPLING OF SOLID WASTES

The initial and perhaps most critical element in a program designed to evaluate the physical and chemical properties of a solid waste is the plan for sampling the waste. It is understandable that analytical studies, with their sophisticated instrumentation and high cost, are often perceived as the dominant element in a waste characterization program. Yet, despite that sophistication and high cost, analytical data generated by a scientifically defective sampling plan have limited utility, particularly in the case of regulatory proceedings.

This section of the manual addresses the development and implementation of a scientifically credible sampling plan for a solid waste and the documentation of the chain of custody for such a plan. The information presented in this section is relevant to the sampling of any solid waste, which has been defined by the EPA in its regulations for the identification and listing of hazardous wastes to include solid, semisolid, liquid, and contained gaseous materials. However, the physical and chemical diversity of those materials, as well as the dissimilar storage facilities (lagoons, open piles, tanks, drums, etc.) and sampling equipment associated with them, preclude a detailed consideration of any specific sampling plan. Consequently, since the burden of responsibility for developing a technically sound sampling plan rests with the waste producer, it is advisable that he seek competent advice before designing a plan. This is particularly true in the early developmental stages of a sampling plan, which require at least a basic understanding of applied statistics. Applied statistics is the science of employing techniques that allow the uncertainty of inductive inferences (general conclusions based on partial knowledge) to be evaluated.

#### 1.1 Development of Appropriate Sampling Plans

An appropriate sampling plan for a solid waste must be responsive to both regulatory and scientific objectives. Once those objectives have been clearly identified, a suitable sampling strategy, predicated upon fundamental statistical concepts, can be developed. The statistical terminology associated with those concepts is reviewed in Table 1.

##### 1.1.1 Regulatory and Scientific Objectives

The EPA, in its hazardous waste management system, has required that certain solid wastes be analyzed for physical and chemical properties. It is mostly chemical properties that are of concern, and, in the case of a number of chemical contaminants, the EPA has promulgated levels (regulatory thresholds) that cannot be equaled or exceeded. The regulations pertaining to the

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TABLE 1. BASIC STATISTICAL TERMINOLOGY APPLICABLE TO SAMPLING PLANS FOR SOLID WASTES

Terminology	Symbol	Mathematical equation	(Equation)
• Variable (e.g., barium or endrin)	X	---	
• Individual measurement of variable	X <sub>i</sub>	---	
• Mean of all possible measurements of variable (population mean)	μ	$\mu = \frac{\sum_{i=1}^N X_i}{N}$ , with N = number of possible measurements	(1)
• Mean of measurements generated by sample (sample mean)	$\bar{x}$	<p><u>Simple random sampling and systematic random sampling</u></p> $\bar{x} = \frac{\sum_{i=1}^n X_i}{n}$ , with n = number of sample measurements	(2a)
		<p><u>Stratified random sampling</u></p> $\bar{x} = \sum_{k=1}^r W_k \bar{x}_k$ , with $\bar{x}_k$ = stratum mean and $W_k$ = fraction of population represented by Stratum k (number of strata [k] ranges from 1 to r)	(2b)
• Variance of sample	s <sup>2</sup>	<p><u>Simple random sampling and systematic random sampling</u></p> $s^2 = \frac{\sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2/n}{n - 1}$	(3a)
		<p><u>Stratified random sampling</u></p> $s^2 = \sum_{k=1}^r W_k s_k^2$ , with $s_k^2$ = stratum variance and $W_k$ = fraction of population represented by Stratum k (number of strata [k] ranges from 1 to r)	(3b)
• Standard deviation of sample	s	$s = \sqrt{s^2}$	(4)
• Standard error (also standard error of mean and standard deviation of mean) of sample	s $\bar{x}$	$s\bar{x} = \frac{s}{\sqrt{n}}$	(5)
• Confidence interval for μ <sup>a</sup>	CI	CI = $\bar{x} \pm t_{.20} s\bar{x}$ , with t <sub>.20</sub> obtained from Table 2 in this section for appropriate degrees of freedom	(6)
• Regulatory threshold <sup>a</sup>	RT	Defined by EPA (e.g., 100 ppm for barium in elutriate of EP toxicity test)	(7)
• Appropriate number of samples to collect from a solid waste (financial constraints not considered)	n	$n = \frac{t_{.20}^2 s^2}{\Delta^2}$ , with Δ = RT - $\bar{x}$	(8)

TABLE 1 (Continued)

Terminology	Symbol	Mathematical equation	(Equation)
• Degrees of freedom	df	$df = n - 1$	(9)
• Square root transformation	---	$\sqrt{X_i + 1/2}$	(10)
• Arcsin transformation	---	$\text{Arcsin}\sqrt{p}$ ; if necessary, refer to any text on basic statistics; measurements must be converted to percentages (p)	(11)

<sup>a</sup>The upper limit of the CI for  $\mu$  is compared to the applicable regulatory threshold (RT) to determine if a solid waste contains the variable (chemical contaminant) of concern at a hazardous level. The contaminant of concern is not considered to be present in the waste at a hazardous level if the upper limit of the CI is less than the applicable RT. Otherwise, the opposite conclusion is reached.

TABLE 2. TABULATED VALUES OF STUDENT'S "t" FOR EVALUATING SOLID WASTES

Degrees of freedom (n-1) <sup>a</sup>	Tabulated "t" value <sup>b</sup>
1	3.078
2	1.886
3	1.638
4	1.533
5	1.476
6	1.440
7	1.415
8	1.397
9	1.383
10	1.372
11	1.363
12	1.356
13	1.350
14	1.345
15	1.341
16	1.337
17	1.333
18	1.330
19	1.328
20	1.325
21	1.323
22	1.321
23	1.319
24	1.318
25	1.316
26	1.315
27	1.314
28	1.313
29	1.311
30	1.310
40	1.303
60	1.296
120	1.289
$\infty$	1.282

<sup>a</sup>Degrees of freedom (df) are equal to the number of samples (n) collected from a solid waste less one.

<sup>b</sup>Tabulated "t" values are for a two-tailed confidence interval and a probability of 0.20 (the same values are applicable to a one-tailed confidence interval and a probability of 0.10).

management of hazardous wastes contain three references regarding the sampling of solid wastes for analytical properties. The first reference, which occurs throughout the regulations, requires that representative samples of waste be collected and defines representative samples as exhibiting average properties of the whole waste. The second reference, which pertains just to petitions to exclude wastes from being listed as hazardous wastes, specifies that enough samples (but in no case less than four samples) be collected over a period of time sufficient to represent the variability of the wastes. The third reference, which applies only to groundwater monitoring systems, mandates that four replicates (subsamples) be taken from each groundwater sample intended for chemical analysis and that the mean concentration and variance for each chemical constituent be calculated from those four subsamples and compared to background levels for groundwater. Even the statistical test to be employed in that comparison is specified (Student's t-test).

The first of the above-described references addresses the issue of sampling accuracy, while the second and third references focus on sampling variability or, conversely, sampling precision (actually the third reference relates to analytical variability, which, in many statistical tests, cannot be distinguished from true sampling variability). Sampling accuracy (the closeness of a sample value to its true value) and sampling precision (the closeness of repeated sample values) are also the issues of overriding importance in any scientific assessment of sampling practices. Thus, from both regulatory and scientific perspectives, the primary objectives of a sampling plan for a solid waste are twofold - namely, to collect samples that will allow sufficiently accurate and precise measurements of the chemical properties of the waste. If the chemical measurements are sufficiently accurate and precise, they will be considered reliable estimates of the chemical properties of the waste.

It is now apparent that a judgment must be made as to the degree of sampling accuracy and precision that is required to reliably estimate the chemical characteristics of a solid waste for the purpose of comparing those characteristics to applicable regulatory thresholds. Generally, high accuracy and high precision are required if one or more chemical contaminants of a solid waste is present at a concentration that is close to the applicable regulatory threshold. Alternatively, relatively low accuracy and low precision can be tolerated if the contaminants of concern occur at levels far below or far above their applicable thresholds. However, a word of caution is in order. Low sampling precision is often associated with considerable savings in analytical, as well as sampling, costs and is clearly recognizable even in the simplest of statistical tests. On the other hand, low sampling accuracy may not entail cost savings and is always obscured (cannot be evaluated) in statistical tests. Therefore, while it is desirable to design sampling plans for solid wastes to achieve only the minimally required precision (at least two samples of a material are required for any estimate of precision), it is prudent to design the plans to attain the greatest possible accuracy.

The roles that inaccurate and imprecise sampling can play in causing a solid waste to be inappropriately judged hazardous are illustrated in Figure 1. When evaluating Figure 1, several points are worthy of consideration. Although a sampling plan for a solid waste generates a mean concentration ( $\bar{x}$ ) and standard deviation ( $s$ , a measure of the extent to which individual sample concentrations are dispersed around  $\bar{x}$ ) for each chemical contaminant of concern, it is not the variation of individual sample concentrations that is of ultimate concern, but rather, the variation that characterizes  $\bar{x}$  itself. That measure of dispersion is termed the standard deviation of the mean (also, the standard error of the mean or standard error) and is designated as  $s_{\bar{x}}$ . Those two sample values,  $\bar{x}$  and  $s_{\bar{x}}$ , are used to estimate the interval (range) within which the true mean ( $\mu$ ) of the chemical concentration probably occurs, assuming that the individual concentrations exhibit a normal (bell-shaped) distribution. For the purposes of evaluating solid wastes, the probability level (confidence interval) of 80% has been selected. That is, for each chemical contaminant of concern, a confidence interval (CI) is described within which  $\mu$  occurs if the sample is representative, which is expected of about 80 out of 100 samples. The upper limit of the 80% CI is then compared to the appropriate regulatory threshold. If the upper limit is less than the threshold, the chemical contaminant is not considered to be present in the waste at a hazardous level; otherwise, the opposite conclusion is drawn. One last point merits explanation. Even if the upper limit of an estimated 80% CI is only slightly less than the regulatory threshold (the worst case of chemical contamination that would be judged acceptable), there is only a 10% (not 20%) chance that the threshold is equaled or exceeded. That is because values of a normally distributed contaminant that are outside the limits of an 80% CI are equally distributed between the left (lower) and right (upper) tails of the normal curve. Consequently, the CI employed to evaluate solid wastes is, for all practical purposes, a 90% interval.

### 1.1.2 Fundamental Statistical Concepts

The concepts of sampling accuracy and precision have already been introduced along with some measurements of central tendency ( $\bar{x}$ ) and dispersion (standard deviation [ $s$ ] and  $s_{\bar{x}}$ ) for concentrations of a chemical contaminant of a solid waste. The utility of  $\bar{x}$  and  $s_{\bar{x}}$  in estimating a confidence interval that probably contains the true mean ( $\mu$ ) concentration of a contaminant has also been described. However, it was noted that the validity of that estimate is predicated upon the assumption that individual concentrations of the contaminant exhibit a normal distribution.

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. Sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population (e.g., every location in a lagoon used to store a solid waste) has a theoretically equal chance of being sampled and measured. Consequently,

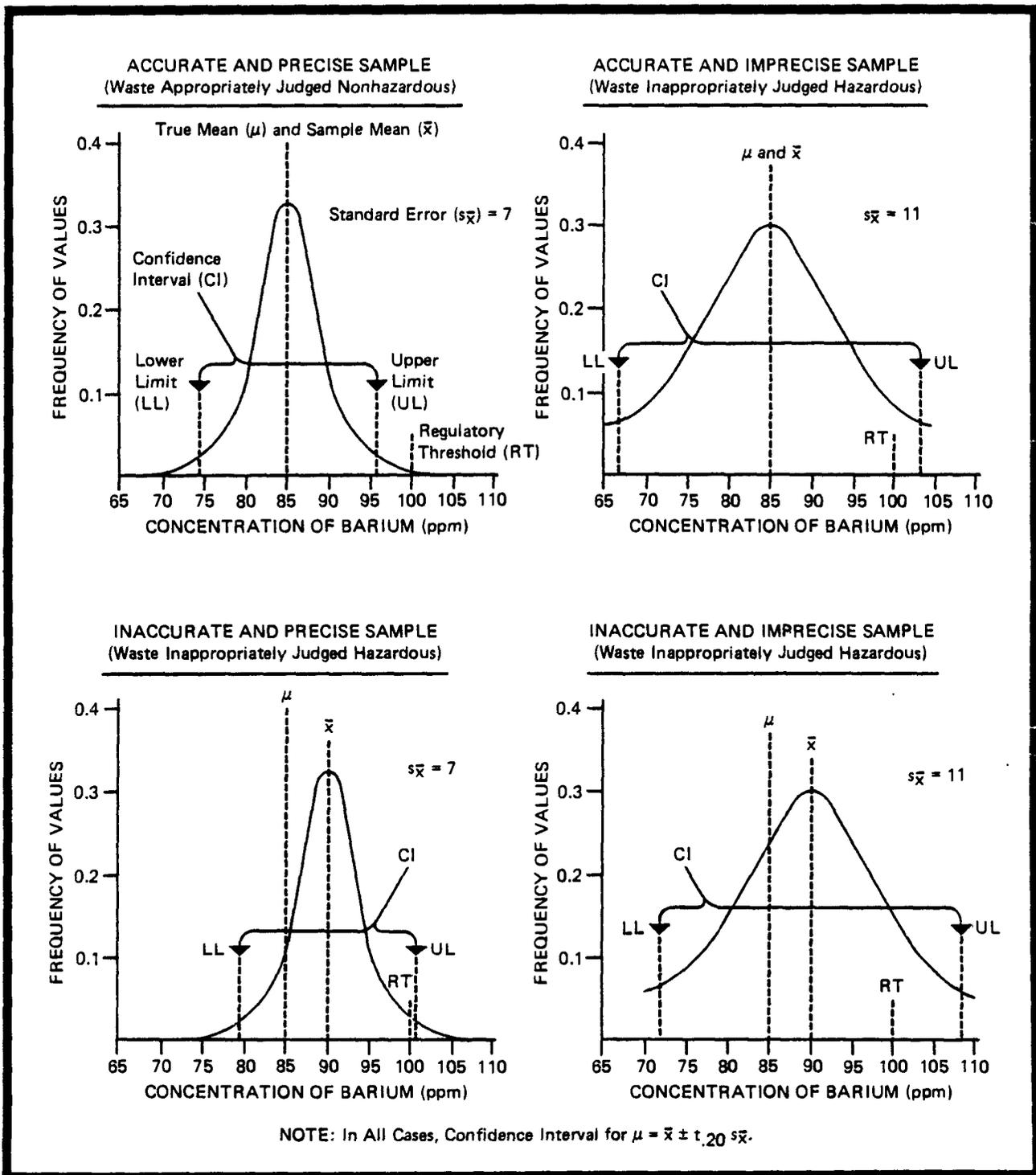


Figure 1.—Important theoretical relationships between sampling accuracy and precision and regulatory objectives for a chemical contaminant of a solid waste that occurs at a concentration marginally less than its regulatory threshold. In this example, barium is the chemical contaminant. The true mean concentration of barium in the elutriate of the EP toxicity test is 85 ppm, as compared to a regulatory threshold of 100 ppm. The upper limit of the confidence interval for the true mean concentration, which is estimated from the sample mean and standard error, must be less than the regulatory threshold if barium is judged to be present in the waste at a nonhazardous level.

statistics generated by the sample (e.g.,  $\bar{x}$ , and, to a lesser degree,  $s_{\bar{x}}$ ) are unbiased (accurate) estimators of true population parameters (e.g., the CI for  $\mu$ ). In other words, the sample is representative of the population. One of the commonest methods of selecting a random sample is to divide the population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers (units) to be sampled through the use of a random numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population.

Sampling precision is most commonly achieved by taking an appropriate number of samples from the population. As can be observed from the equation for calculating  $s_{\bar{x}}$ , precision increases ( $s_{\bar{x}}$  and the CI for  $\mu$  decrease) as the number of samples ( $n$ ) increases, although not in a 1:1 ratio. For example, a 100% increase in the number of samples from two to four causes the CI to decrease by approximately 62% (about 31% of that decrease is associated with the critical upper tail of the normal curve). However, another 100% increase in sampling effort from four to eight samples results in only an additional 39% decrease in the CI. Another technique for increasing sampling precision is to maximize the physical size (weight or volume) of the samples that are collected. That has the effect of minimizing between-sample variation and, consequently, decreasing  $s_{\bar{x}}$ . Increasing the number or size of samples taken from a population, in addition to increasing sampling precision, has the secondary effect of increasing sampling accuracy.

In summary, reliable information concerning the chemical properties of a solid waste is needed for the purpose of comparing those properties to applicable regulatory thresholds. If chemical information is to be considered reliable, it must be accurate and sufficiently precise. Accuracy is usually achieved by incorporating some form of randomness into the selection process for the samples that generate the chemical information. Sufficient precision is most often obtained by selecting an appropriate number of samples.

There are a few ramifications of the above-described concepts that merit elaboration. If, for example, as in the case of semiconductor etching solutions, each batch of a waste is completely homogeneous with regard to the chemical properties of concern and that chemical homogeneity is constant (uniform) over time (from batch to batch), a single sample collected from the waste at an arbitrary location and time would theoretically generate an accurate and precise estimate of the chemical properties. However, most wastes are heterogeneous in terms of their chemical properties. If a batch of waste is randomly heterogeneous with regard to its chemical characteristics and that random chemical heterogeneity remains constant from batch to batch, accuracy and appropriate precision can usually be achieved by simple random sampling. In that type of sampling, all units in the population

(essentially all locations or points in all batches of waste from which a sample could be collected) are identified, and a suitable number of samples is randomly selected from the population. More complex stratified random sampling is appropriate if a batch of waste is known to be nonrandomly heterogeneous in terms of its chemical properties and/or nonrandom chemical heterogeneity is known to exist from batch to batch. In such cases, the population is stratified to isolate the known sources of nonrandom chemical heterogeneity. After stratification, which may occur over space (locations or points in a batch of waste) and/or time (each batch of waste), the units in each stratum are numerically identified, and a simple random sample is taken from each stratum. As previously intimated, both simple and stratified random sampling generate accurate estimates of the chemical properties of a solid waste. The advantage of stratified random sampling over simple random sampling is that, for a given number of samples and a given sample size, the former technique often results in a more precise estimate of chemical properties of a waste (a lower value of  $s_{\bar{x}}$ ) than the latter technique. However, greater precision is likely to be realized only if a waste exhibits substantial nonrandom chemical heterogeneity and stratification efficiently "divides" the waste into strata that exhibit maximum between-strata variability and minimum within-strata variability. If that does not occur, stratified random sampling can produce results that are less precise than in the case of simple random sampling. Therefore, it is reasonable to select stratified random sampling over simple random sampling only if the distribution of chemical contaminants in a waste is sufficiently known to allow an intelligent identification of strata and at least two or three samples can be collected in each stratum. If a strategy employing stratified random sampling is selected, a decision must be made regarding the allocation of sampling effort among strata. When chemical variation within each stratum can be estimated with a great degree of detail, samples should be optimally allocated among strata, i.e., the number of samples collected from each stratum should be directly proportional to the chemical variation encountered in the stratum. When detailed information concerning chemical variability within strata is not available, samples should be proportionally allocated among strata, i.e., sampling effort in each stratum should be directly proportional to the size of the stratum.

Simple random sampling and stratified random sampling are types of probability sampling, which, because of a reliance upon mathematical and statistical theories, allows an evaluation of the effectiveness of sampling procedures. Another type of probability sampling is systematic random sampling, in which the first unit to be collected from a population is randomly selected, but all subsequent units are taken at fixed space or time intervals. An example of systematic random sampling is the sampling of a waste lagoon along a transect in which the first sampling point on the transect is 1 m from a randomly selected location on the shore and subsequent sampling points are located at 2-m intervals along the transect. The advantages of systematic random sampling over simple random sampling and stratified random sampling are the ease in which samples are identified and collected (the selection of the first sampling unit determines the remainder

of the units) and, sometimes, an increase in precision. In certain cases, for example, systematic random sampling might be expected to be a little more precise than stratified random sampling with one unit per stratum because samples are distributed more evenly over the population. As will be demonstrated shortly, disadvantages of systematic random sampling are the poor accuracy and precision that can occur when unrecognized trends or cycles occur in the population. For those reasons, systematic random sampling is recommended only when a population is essentially random or contains at most a modest stratification. In such cases, systematic random sampling would be employed for the sake of convenience, with little expectation of an increase in precision over other random sampling techniques.

Probability sampling is contrasted with authoritative sampling, in which an individual who is well acquainted with the solid waste to be sampled selects a sample without regard to randomization. The validity of data gathered in that manner is totally dependent on the knowledge of the sampler and, although valid data can sometimes be obtained, authoritative sampling is not recommended for the chemical characterization of most wastes.

It may now be useful to offer a generalization regarding the four sampling strategies that have been identified for solid wastes. If little or no information is available concerning the distribution of chemical contaminants of a waste, simple random sampling is the most appropriate sampling strategy. As more information is accumulated for the contaminants of concern, greater consideration can be given (in order of the additional information required) to stratified random sampling, systematic random sampling, and, perhaps, authoritative sampling.

The validity of a CI for the true mean ( $\mu$ ) concentration of a chemical contaminant of a solid waste is, as previously noted, based on the assumption that individual concentrations of the contaminant exhibit a normal distribution. This is true regardless of the strategy that is employed to sample the waste. Although there are computational procedures for evaluating the correctness of the assumption of normality, those procedures are meaningful only if a large number of samples are collected from a waste. Since sampling plans for most solid wastes entail just a few samples, one can do little more than superficially examine resulting data for obvious departures from normality (this can be done by simple graphical methods), keeping in mind that even if individual measurements of a chemical contaminant of a waste exhibit a considerably abnormal distribution, such abnormality is not likely to be the case for sample means, which are our primary concern. One can also compare the mean of the sample ( $\bar{x}$ ) to the variance of the sample ( $s^2$ ). In a normally distributed population,  $\bar{x}$  would be expected to be greater than  $s^2$  (assuming that the number of samples [ $n$ ] is reasonably large). If that is not the case, the chemical contaminant of concern may be characterized by a Poisson distribution ( $\bar{x}$  is approximately equal to  $s^2$ ) or a negative binomial distribution ( $\bar{x}$  is less than  $s^2$ ). In the former circumstance, normality can often be achieved by transforming data according to the square root transformation. In the latter circumstance, normality may be realized through use of the arcsine transformation.

If either transformation is required, all subsequent statistical evaluations must be performed on the transformed scale.

Finally, it is necessary to address the appropriate number of samples to be employed in the chemical characterization of a solid waste. As has already been emphasized, the appropriate number of samples is the least number of samples required to generate a sufficiently precise estimate of the true mean ( $\mu$ ) concentration of a chemical contaminant of a waste. From the perspective of most waste producers, that means the minimal number of samples needed to demonstrate that the upper limit of the CI for  $\mu$  is less than the applicable regulatory threshold (RT). The formula for estimating appropriate sampling effort (Table 1, Equation 8) indicates that increased sampling effort is generally justified as  $s^2$  or the "t<sub>.20</sub>" value (probable error rate) increases and as  $\Delta (RT - \bar{x})$  decreases. In a well-designed sampling plan for a solid waste, an effort is made to estimate the values of  $\bar{x}$  and  $s^2$  before sampling is initiated. Such preliminary estimates, which may be derived from information pertaining to similar wastes, process engineering data, or limited analytical studies, are used to identify the approximate number of samples that must be collected from the waste. It is always prudent to collect a somewhat greater number of samples than indicated by preliminary estimates of  $\bar{x}$  and  $s^2$  since poor preliminary estimates of those statistics can result in an underestimate of the appropriate number of samples to collect. It is usually possible to appropriately process and store the extra samples until analysis of the initially identified samples is completed and it can be determined if analysis of the additional samples is warranted.

### 1.1.3 Basic Sampling Strategies

It is now appropriate to present general procedures for implementing the three previously introduced sampling strategies (simple random sampling, stratified random sampling, and systematic random sampling) and a hypothetical example of each sampling strategy. The hypothetical examples illustrate the statistical calculations that must be performed in most situations likely to be encountered by a waste producer and, also, provide some insight into the efficiency of the three sampling strategies in meeting regulatory objectives.

The following hypothetical conditions are assumed to exist for all three sampling strategies. First, barium, which has a RT of 100 ppm as measured in the EP elutriate test, is the only chemical contaminant of concern. Second, barium is discharged in particulate form to a waste lagoon and accumulates in the lagoon in the form of a sludge, which has built up to approximately the same thickness throughout the lagoon. Third, concentrations of barium are relatively homogeneous along the vertical gradient (from the water-sludge interface to the sludge-lagoon interface), suggesting a highly controlled manufacturing process (little between-batch variation in barium concentrations).

Fourth, the physical size of sludge samples collected from the lagoon is as large as practical, and barium concentrations derived from those samples are normally distributed (note that we do not refer to barium levels in the samples of sludge since barium measurements are actually made on the elutriate from EP toxicity tests performed with the samples). Last, a preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago identified values of 86 and 90 ppm for material collected near the outfall (in the upper third) of the lagoon and values of 98 and 104 ppm for material obtained from the far end (the lower two-thirds) of the lagoon.

For all sampling strategies, it is important to remember that barium will be determined to be present in the sludge at a hazardous level if the upper limit of the CI for  $\mu$  is equal to or greater than the RT of 100 ppm (Table 1, Equations 6 and 7).

#### 1.1.3.1 Simple Random Sampling

Simple random sampling (Box 1) is performed by general procedures in which preliminary estimates of  $\bar{x}$  and  $s^2$ , as well as a knowledge of the RT, for each chemical contaminant of a solid waste that is of concern are employed to estimate the appropriate number of samples ( $n$ ) to be collected from the waste. That number of samples is subsequently analyzed for each chemical contaminant of concern. The resulting analytical data are then used to definitively conclude that each contaminant is or is not present in the waste at a hazardous concentration or, alternatively, to suggest a reiterative process, involving increased sampling effort, through which the presence or absence of hazard can be definitively determined.

In the hypothetical example for simple random sampling (Box 1), preliminary estimates of  $\bar{x}$  and  $s^2$  indicated a sampling effort consisting of six samples. That number of samples was collected and initially analyzed, generating analytical data somewhat different from the preliminary data ( $s^2$  was substantially greater than was preliminarily estimated). Consequently, the upper limit of the CI was unexpectedly greater than the applicable RT, resulting in a tentative conclusion of hazard. However, a reestimation of appropriate sampling effort, based on statistics derived from the six samples, suggested that such a conclusion might be reversed through the collection and analysis of just one more sample. Fortunately, a resampling effort was not required because of the foresight of the waste producer in obtaining three extra samples during the initial sampling effort, which, because of their influence in decreasing the final values of  $\bar{x}$ ,  $s_{\bar{x}}^2$ ,  $t_{.20}$ , and, consequently, the upper limit of the CI - values obtained from all nine samples - resulted in a definitive conclusion of nonhazard.

BOX 1. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SIMPLE RANDOM SAMPLING OF WASTES

<u>Step</u>	<u>General Procedures</u>
1.	Obtain preliminary estimates of $\bar{x}$ and $s^2$ for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2a and 3a (Table 1).
2.	Estimate the appropriate number of samples ( $n_1$ ) to be collected from the waste through use of Equation 8 (Table 1) and Table 2. Derive individual values of $n_1$ for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual $n_1$ values.
3.	Randomly collect at least $n_1$ samples (or $n_2 - n_1$ , $n_3 - n_2$ , etc. samples, as will be indicated later in this box) from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and $s^2$ ). Maximize the physical size (weight or volume) of all samples that are collected.
4.	Analyze the $n_1$ (or $n_2 - n_1$ , $n_3 - n_2$ , etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data for obvious departures from normality.
5.	Calculate $\bar{x}$ , $s^2$ , the standard deviation ( $s$ ), and $s_{\bar{x}}$ for each set of analytical data by, respectively, Equations 2a, 3a, 4, and 5 (Table 1).
6.	If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7; Table 1) and is believed to be an accurate estimator of $\mu$ , the contaminant is considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than $s^2$ , perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to $s^2$ ) or the arcsine transformation (if $\bar{x}$ is less than $s^2$ ) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 1).
7.	Determine the CI for each chemical contaminant of concern by Equation 6 (Table 1) and Table 2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7; Table 1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, the opposite conclusion is tentatively reached.

8. If a tentative conclusion of hazard is reached, reestimate the total number of samples ( $n_2$ ) to be collected from the waste by use of Equation 8 (Table 1) and Table 2. When deriving  $n_2$ , employ the newly calculated (not preliminary) values of  $\bar{x}$  and  $s^2$ . If an additional  $n_2 - n_1$  samples of waste cannot reasonably be collected, the study is completed and a definitive conclusion of hazard is reached. Otherwise, collect an extra  $n_2 - n_1$  samples of waste.
9. Repeat the basic operations described in Steps 3-8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, increased sampling effort is impractical.

### Hypothetical Example

#### Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are not judged to be indicative of nonrandom chemical heterogeneity (stratification) within the lagoon. Therefore, preliminary estimates of  $\bar{x}$  and  $s^2$  are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^n X_i}{n} = \frac{86 + 90 + 98 + 104}{4} = 94.50, \text{ and} \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2/n}{n - 1} \quad (\text{Equation 3a})$$

$$= \frac{35,916.00 - 35,721.00}{3} = 65.00.$$

2. Based on the preliminary estimates of  $\bar{x}$  and  $s^2$ , as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t^2 \cdot 20s^2}{\Delta^2} = \frac{(1.638^2)(65.00)}{5.50^2} = 5.77. \quad (\text{Equation 8})$$

3. As indicated above, the appropriate number of sludge samples ( $n_1$ ) to be collected from the lagoon is six. That number of samples (plus three extra samples for protection against poor preliminary estimates of  $\bar{x}$  and  $s^2$ ) is collected from the lagoon by a single randomization process (Figure 2). All samples consist of the greatest volume of sludge that can be practically collected. The three extra samples are suitably processed and stored for possible later analysis.
4. The six samples of sludge ( $n_1$ ) designated for immediate analysis generate the following concentrations of barium in the EP toxicity test: 89, 90, 87, 96, 93, and 113 ppm. Although the value of 113 ppm appears unusual as compared to the other data, there is no obvious indication that the data are not normally distributed.
5. New values for  $\bar{x}$  and  $s^2$  and associated values for the standard deviation ( $s$ ) and  $s_{\bar{x}}$  are calculated as:

$$\bar{x} = \frac{\sum_{i=1}^n X_i}{n} = \frac{89 + 90 + 87 + 96 + 93 + 113}{6} = 94.67, \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2/n}{n - 1} \quad (\text{Equation 3a})$$

$$= \frac{54,224.00 - 53,770.67}{5} = 90.67,$$

$$s = \sqrt{s^2} = 9.52, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 9.52/\sqrt{6} = 3.89. \quad (\text{Equation 5})$$

6. The new value for  $\bar{x}$  (94.67) is less than the RT (100). In addition,  $\bar{x}$  is greater (only slightly) than  $s^2$  (90.67) and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculations performed with nontransformed data.
7.  $CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 94.67 \pm (1.476)(3.89) \quad (\text{Equation 6})$   
 $= 94.67 \pm 5.74.$

Since the upper limit of the CI (100.41) is greater than the applicable RT (100), it is tentatively concluded that barium is present in the sludge at a hazardous concentration.

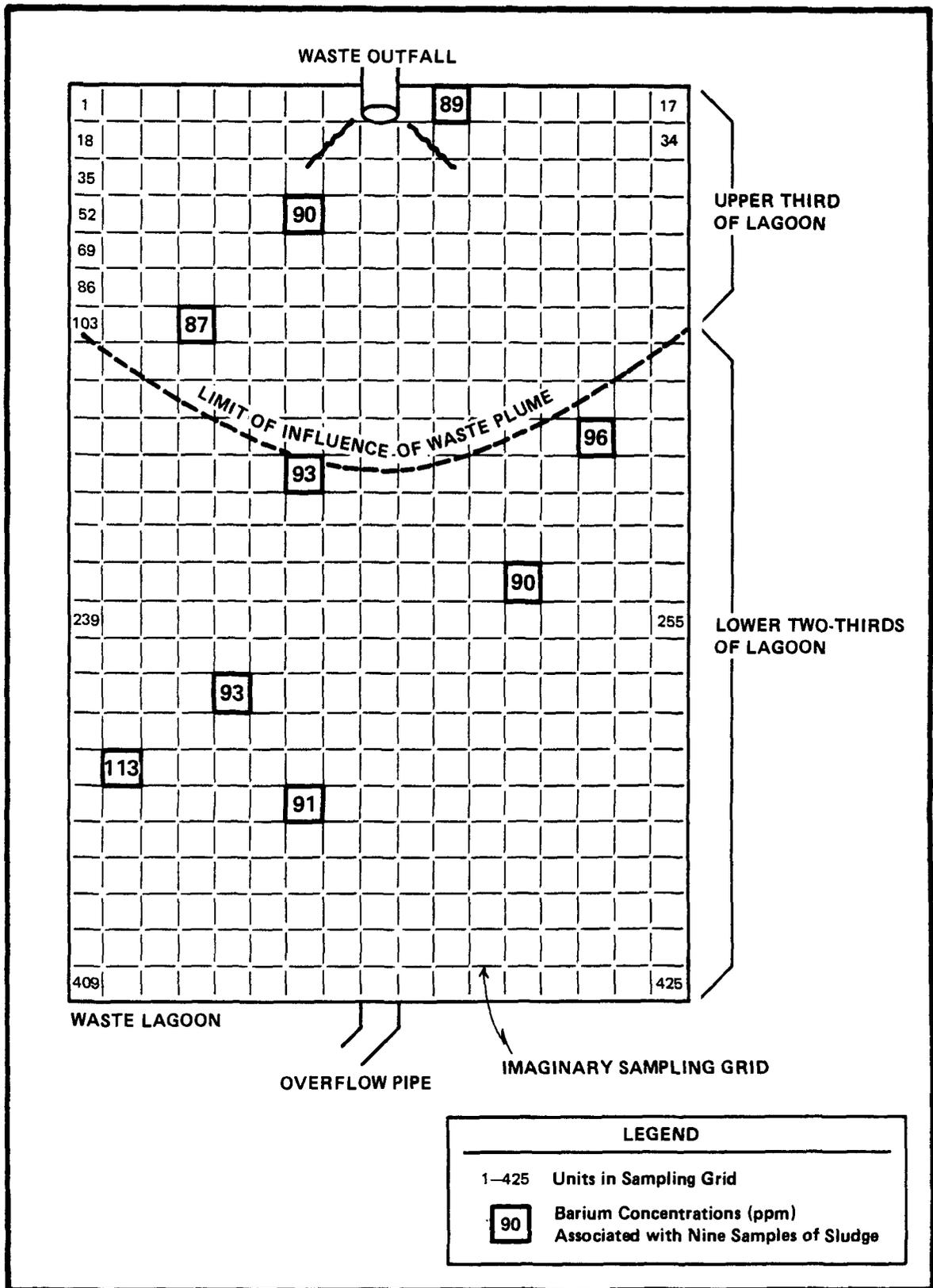


Figure 2.—Hypothetical sampling conditions in waste lagoon containing sludge contaminated with barium. Barium concentrations associated with samples of sludge refer to levels measured in the elutriate of EP toxicity tests conducted with the samples.

8.  $n$  is now reestimated as:

$$n_2 = \frac{t_{.20}^2 s^2}{\Delta^2} \frac{(1.476^2)(90.67)}{5.33^2} = 6.95. \quad (\text{Equation 8})$$

The value for  $n_2$  ( $\sim 7$ ) indicates that an additional ( $n_2 - n_1 = 1$ ) sludge sample should be collected from the lagoon.

9. The additional sampling effort is not necessary because of the three extra samples that were initially collected from the lagoon. All extra samples are analyzed, generating the following levels of barium for the EP toxicity test: 93, 90, and 91 ppm. Consequently,  $\bar{x}$ ,  $s^2$ , the standard deviation ( $s$ ), and  $s_{\bar{x}}$  are recalculated as:

$$\bar{x} = \frac{\sum_{i=1}^n X_i}{n} = \frac{89 + 90 + \dots + 91}{9} = 93.56, \quad (\text{Equation 2a})$$

$$s^2 = \frac{\sum_{i=1}^n X_i^2 - (\sum_{i=1}^n X_i)^2/n}{n - 1} \quad (\text{Equation 3a})$$

$$= \frac{79,254.00 - 78,773.78}{8} = 60.03,$$

$$s = \sqrt{s^2} = 7.75, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.75/\sqrt{9} = 2.58. \quad (\text{Equation 5})$$

The value for  $\bar{x}$  (93.56) is again less than the RT (100), and there is no indication that the nine data points, considered collectively, are abnormally distributed (in particular,  $\bar{x}$  is now substantially greater than  $s^2$ ). Consequently, CI, calculated with nontransformed data, is determined to be:

$$\begin{aligned} \text{CI} &= \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.58) \quad (\text{Equation 6}) \\ &= 93.56 \pm 3.60. \end{aligned}$$

The upper limit of the CI (97.16) is now less than the RT of 100. Consequently, it is definitively concluded that barium is not present in the sludge at a hazardous level.

### 1.1.3.2 Stratified Random Sampling

Stratified random sampling (Box 2) is conducted by general procedures that are similar to the procedures described for simple random sampling. The only difference is that, in stratified random sampling, values of  $\bar{x}$  and  $s^2$  are calculated for each stratum in the population and then integrated into overall estimates of those statistics, the standard deviation ( $s$ ),  $s_{\bar{x}}$ , and the appropriate number of samples ( $n$ ) for all strata.

The hypothetical example for stratified random sampling (Box 2) is based on the same nine sludge samples previously identified in the example of simple random sampling (Box 1) so that the relative efficiencies of the two sampling strategies can be fully compared. The efficiency generated through the process of stratification is first evident in the preliminary estimate of  $n$  (Step 2 in Boxes 1 and 2), which is six for simple random sampling and four for stratified random sampling. (The lesser value for stratified sampling is the consequence of a dramatic decrease in  $s^2$ , which more than compensated for a modest increase in  $\Delta$ .) The most relevant indication of sampling efficiency is the value of  $s_{\bar{x}}$ , which is directly employed to calculate the CI. In the case of simple random sampling,  $s_{\bar{x}}$  is calculated as 2.58 (Step 9 in Box 1), while, for stratified random sampling,  $s_{\bar{x}}$  is determined to be 2.35 (Steps 5 and 7 in Box 2). Consequently, the gain in efficiency attributable to stratification is approximately 9% ( $0.23/2.58$ ).

### 1.1.3.3 Systematic Random Sampling

Systematic random sampling (Box 3) is implemented by general procedures that are identical to the procedures identified for simple random sampling. The hypothetical example for systematic random sampling (Box 3) demonstrates the bias and imprecision that are associated with that type of sampling when unrecognized trends or cycles exist in the population.

### 1.1.4 Special Considerations

The preceding discussion has addressed the major issues that are critical to the development of a reliable sampling strategy for a solid waste. The remaining discussion focuses on several "secondary" issues that should be considered when designing an appropriate sampling strategy. These secondary issues are applicable to all three of the basic sampling strategies that have been identified.

BOX 2. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - STRATIFIED RANDOM SAMPLING OF WASTES

<u>Step</u>	<u>General Procedures</u>
1.	Obtain preliminary estimates of $\bar{x}$ and $s^2$ for each chemical contaminant of a solid waste that is of concern. The two above-identified statistics are calculated by, respectively, Equations 2b and 3b (Table 1).
2.	Estimate the appropriate number of samples ( $n_1$ ) to be collected from the waste through use of Equation 8 (Table 1) and Table 2. Derive individual values of $n_1$ for each chemical contaminant of concern. The appropriate number of samples to be taken from the waste is the greatest of the individual $n_1$ values.
3.	Randomly collect at least $n_1$ samples (or $n_2 - n_1$ , $n_3 - n_2$ , etc. samples, as will be indicated later in this box) from the waste (collection of a few extra samples will provide protection against poor preliminary estimates of $\bar{x}$ and $s^2$ ). If $s_k$ for each stratum (see Equation 3b) is believed to be an accurate estimate, optimally allocate samples among strata (i.e., allocate samples among strata so that the number of samples collected from each stratum is directly proportional to $s_k$ for that stratum). Otherwise, proportionally allocate samples among strata according to size of the strata. Maximize the physical size (weight or volume) of all samples that are collected from the strata.
4.	Analyze the $n_1$ (or $n_2 - n_1$ , $n_3 - n_2$ , etc.) samples for each chemical contaminant of concern. Superficially (graphically) examine each set of analytical data from each stratum for obvious departures from normality.
5.	Calculate $\bar{x}$ , $s^2$ , the standard deviation ( $s$ ), and $s\bar{x}$ for each set of analytical data by, respectively, Equations 2b, 3b, 4, and 5 (Table 1).
6.	If $\bar{x}$ for a chemical contaminant is equal to or greater than the applicable RT (Equation 7; Table 1) and is believed to be an accurate estimator of $\mu$ , the contaminant is considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, continue the study. In the case of a set of analytical data that does not exhibit obvious abnormality and for which $\bar{x}$ is greater than $s^2$ , perform the following calculations with nontransformed data. Otherwise, consider transforming the data by the square root transformation (if $\bar{x}$ is about equal to $s^2$ ) or the arcsine transformation (if $\bar{x}$ is less than $s^2$ ) and performing all subsequent calculations with transformed data. Square root and arcsine transformations are defined by, respectively, Equations 10 and 11 (Table 1).

7. Determine the CI for each chemical contaminant of concern by Equation 6 (Table 1) and Table 2. If the upper limit of the CI is less than the applicable RT (Equations 6 and 7; Table 1), the chemical contaminant is not considered to be present in the waste at a hazardous concentration and the study is completed. Otherwise, the opposite conclusion is tentatively reached.
8. If a tentative conclusion of hazard is reached, reestimate the total number of samples ( $n_2$ ) to be collected from the waste by use of Equation 8 (Table 1) and Table 2. When deriving  $n_2$ , employ the newly calculated (not preliminary) values of  $\bar{x}$  and  $s^2$ . If an additional  $n_2 - n_1$  samples of waste cannot reasonably be collected, the study is completed and a definitive conclusion of hazard is reached. Otherwise, collect an extra  $n_2 - n_1$  samples of waste.
9. Repeat the basic operations described in Steps 3-8 until the waste is judged to be nonhazardous or, if the opposite conclusion continues to be reached, increased sampling effort is impractical.

#### Hypothetical Example

##### Step

1. The preliminary study of barium levels in the elutriate of four EP toxicity tests conducted with sludge collected from the lagoon several years ago generated values of 86 and 90 ppm for sludge obtained from the upper third of the lagoon and values of 98 and 104 ppm for sludge from the lower two-thirds of the lagoon. Those two sets of values are judged to be indicative of nonrandom chemical heterogeneity (two strata) within the lagoon. Therefore, preliminary estimates of  $\bar{x}$  and  $s^2$  are calculated as:

$$\bar{x} = \sum_{k=1}^r W_k \bar{x}_k = \frac{(1)(88.00)}{3} + \frac{(2)(101.00)}{3} = 96.67, \text{ and} \quad (\text{Equation 2b})$$

$$s^2 = \sum_{k=1}^r W_k s_k^2 = \frac{(1)(8.00)}{3} + \frac{(2)(18.00)}{3} = 14.67. \quad (\text{Equation 3b})$$

2. Based on the preliminary estimates of  $\bar{x}$  and  $s^2$ , as well as the knowledge that the RT for barium is 100 ppm,

$$n_1 = \frac{t_{.20}^2 s^2}{\Delta^2} = \frac{(1.368^2)(14.67)}{3.33^2} = 3.55. \quad (\text{Equation 8})$$

3. As indicated above, the appropriate number of sludge samples ( $n_1$ ) to be collected from the lagoon is four. However, for purposes of comparison to simple random sampling (Box 1), six samples (plus three extra samples for protection against poor preliminary estimates of  $\bar{x}$  and  $s^2$ ) are collected from the lagoon by a two-stage randomization process (Figure 2). Because  $s_k$  for the upper (2.12 ppm) and lower (5.66 ppm) strata are not believed to be very accurate estimates, the nine samples to be collected from the lagoon are not optimally allocated between the two strata (optimum allocation would require two and seven samples to be collected from the upper and lower strata, respectively). Alternatively, proportional allocation is employed - three samples are collected from the upper stratum (which represents one-third of the lagoon), and six samples are taken from the lower stratum (two-thirds of the lagoon). All samples consist of the greatest volume of sludge that can be practically collected.
4. The nine samples of sludge generate the following concentrations of barium in the EP toxicity test: upper stratum - 89, 90, and 87 ppm; lower stratum - 96, 93, 113, 93, 90, and 91 ppm. Although the value of 113 ppm appears unusual as compared to other data for the lower stratum, there is no obvious indication that the data are not normally distributed.
5. New values for  $\bar{x}$  and  $s^2$  and associated values for the standard deviation ( $s$ ) and  $s_{\bar{x}}$  are calculated as:

$$\bar{x} = \sum_{k=1}^r W_k \bar{x}_k = \frac{(1)(88.67)}{3} + \frac{(2)(96.00)}{3} = 93.56, \quad (\text{Equation 2b})$$

$$s^2 = \sum_{k=1}^r W_k s_k^2 = \frac{(1)(2.33)}{3} + \frac{(2)(73.60)}{3} = 49.84, \quad (\text{Equation 3b})$$

$$s = \sqrt{s^2} = 7.06, \text{ and} \quad (\text{Equation 4})$$

$$s_{\bar{x}} = s/\sqrt{n} = 7.06/\sqrt{9} = 2.35. \quad (\text{Equation 5})$$

6. The new value for  $\bar{x}$  (93.56) is less than the RT (100). In addition,  $\bar{x}$  is greater than  $s^2$  (49.84) and, as previously indicated, the raw data are not characterized by obvious abnormality. Consequently, the study is continued, with the following calculation performed with nontransformed data.
7.  $CI = \bar{x} \pm t_{.20} s_{\bar{x}} = 93.56 \pm (1.397)(2.35) \quad (\text{Equation 6})$   
 $= 93.56 \pm 3.28.$

The upper limit of the CI (96.84) is less than the applicable RT (100). Therefore, it is concluded that barium is not present in the sludge at a hazardous concentration.

BOX 3. STRATEGY FOR DETERMINING IF CHEMICAL CONTAMINANTS OF SOLID WASTES ARE PRESENT AT HAZARDOUS LEVELS - SYSTEMATIC RANDOM SAMPLING

<u>Step</u>	<u>General Procedure</u>
1.	Follow general procedures presented for simple random sampling of solid wastes (Box 1).
<u>Step</u>	<u>Hypothetical Example</u>
1.	The example presented in Box 1 is applicable to systematic random sampling with the understanding that the nine sludge samples obtained from the lagoon would be collected at equal intervals along a transect running from a randomly selected location on one bank of the lagoon to the opposite bank. If that randomly selected transect were established between Units 1 and 409 of the sampling grid (Figure 2) and sampling were performed at Unit 1 and, thereafter, at three-unit intervals along the transect (i.e., Unit 1, Unit 52, Unit 103, . . . , and Unit 409), it is apparent that only two samples would be collected in the upper third of the lagoon, while seven samples would be obtained from the lower two-thirds of the lagoon. If, as suggested by the barium concentrations illustrated in Figure 2, the lower part of the lagoon is characterized by greater and more variable barium contamination than the upper part of the lagoon, systematic random sampling along the above-identified transect, by placing undue (disproportionate) emphasis on the lower part of the lagoon, might be expected to result in an inaccurate (overestimation) and imprecise characterization of barium levels in the whole lagoon, as compared to either simple random sampling or stratified random sampling. Such inaccuracy and imprecision, which is typical of systematic random sampling when unrecognized trends or cycles occur in the population, would be magnified if, for example, the randomly selected transect were established solely in the lower part of the lagoon, e.g., between Units 239 and 255 of the sampling grid.

#### 1.1.4.1 Composite Sampling

In composite sampling, a number of random samples are initially collected from a waste and combined into a single sample, which is then analyzed for the chemical contaminants of concern. The major disadvantage of composite sampling as compared to noncomposite sampling is that information concerning the chemical contaminants is lost, i.e., each initial set of samples generates only a single estimate of the concentration of each contaminant. Consequently, since the number of analytical measurements ( $n$ ) is small,  $s_{\bar{x}}$  and  $t_{.20}$  are large, thus decreasing the likelihood that a contaminant will be judged to occur in the waste at a nonhazardous level (refer to appropriate equations in Table 1 and to Table 2). A remedy to that situation is to collect and analyze a relatively large number of composite samples, thereby offsetting the savings in analytical costs that are often associated with composite sampling, but achieving better representation of the waste than would occur with noncomposite sampling.

The appropriate number of composite samples to be collected from a solid waste is estimated by use of Equation 8 (Table 1) as previously described for the three basic sampling strategies. In comparison to noncomposite sampling, composite sampling may have the effect of minimizing between-sample variation (the same phenomenon that occurs when the physical size of a sample is maximized), thereby reducing somewhat the number of samples that must be collected from the waste.

#### 1.1.4.2 Subsampling

The variance ( $s^2$ ) associated with a chemical contaminant of a waste consists of two components in that:

$$s^2 = s_s^2 + \frac{s_a^2}{m}, \quad (\text{Equation 12})$$

with  $s_s^2$  = a component attributable to sampling (sample) variation,  $s_a^2$  = a component attributable to analytical (subsample) variation, and  $m$  = number of subsamples. In general,  $s_a^2$  should not be allowed to exceed one-ninth of  $s_s^2$ . If a preliminary study indicates that  $s_a^2$  exceeds that threshold, a sampling strategy involving subsampling should be considered. In such a strategy, a number of replicate measurements are randomly made on a relatively limited number of randomly collected samples. Consequently, analytical effort is allocated as a function of analytical variability. The efficiency of that general strategy in meeting regulatory objectives has already been demonstrated in the previous discussions of sampling effort.

The appropriate number of samples ( $n$ ) to be collected from a solid waste for which subsampling will be employed is again estimated by Equation 8 (Table 1). In the case of simple random sampling or systematic random sampling with an equal number of subsamples analyzed per sample:

$$\bar{\bar{x}} = \frac{\sum_{i=1}^n \bar{x}_i}{n}, \quad (\text{Equation 13})$$

with  $\bar{x}_i$  = sample mean (calculated from values for subsamples) and  $n$  = number of samples. Also,

$$s^2 = \frac{\sum_{i=1}^n \bar{x}_i^2 - (\sum_{i=1}^n \bar{x}_i)^2/n}{n - 1}. \quad (\text{Equation 14})$$

The optimum number of subsamples to be taken from each sample ( $m_{\text{opt.}}$ ) is estimated as:

$$m(\text{opt.}) = \frac{s_a}{s_s} \quad (\text{Equation 15})$$

when cost factors are not considered. The value for  $s_a$  is calculated from available data as:

$$s_a = \sqrt{\frac{\sum_{i=1}^n \sum_{j=1}^m x_{ij}^2 - (\sum_{i,j} x_{ij})^2/m}{n(m-1)}}, \quad (\text{Equation 16})$$

and  $s_s$ , which can have a negative characteristic, is defined as:

$$s_s = \sqrt{s^2 - \frac{s_a^2}{m}}, \quad (\text{Equation 17})$$

with  $s^2$  calculated as indicated in Equation 14.

In the case of stratified random sampling with subsampling, critical formulas for estimating sample size ( $n$ ) by Equation 8 (Table 1) are:

$$\bar{\bar{x}} = \frac{\sum_{k=1}^r W_k \bar{x}_k}{r}, \quad (\text{Equation 2b})$$

with  $\bar{x}_k$  = stratum mean and  $W_k$  = fraction of population represented by Stratum K (number of strata, k, ranges from 1 to r). In Equation 2b,  $\bar{x}_k$  for each stratum is calculated as the average of all sample means in the stratum (sample means are calculated from values for subsamples). In addition:

$$s^2 = \sum_{k=1}^r W_k s_k^2, \quad (\text{Equation 3b})$$

with  $s_k^2$  for each stratum calculated from all sample means in the stratum. The optimum subsampling effort when cost factors are not considered and all replication is symmetrical is again estimated as:

$$m(\text{opt.}) = \frac{s_a}{s_s}, \quad \text{with} \quad (\text{Equation 15})$$

$$s_a = \sqrt{\frac{\sum_{k=1}^r \sum_{i=1}^n \sum_{j=1}^m x_{kij}^2 - (\sum x_{kij})^2/m}{rn(m-1)}}, \quad \text{and} \quad (\text{Equation 18})$$

$$s_s = \sqrt{\frac{s^2 - s_a^2}{m}}, \quad (\text{Equation 17})$$

with  $s^2$  derived as shown in Equation 3b.

#### 1.1.4.3 Cost and Loss Functions

The cost of chemically characterizing a waste is dependent on the specific strategy that is employed to sample the waste. For example, in the case of simple random sampling without subsampling, a reasonable cost function might be:

$$C(n) = C_0 + C_1 n, \quad (\text{Equation 19})$$

with  $C(n)$  = cost of employing a sample size of n,  $C_0$  = an overhead cost (which is independent of the number of samples that are collected and analyzed), and  $C_1$  = a sample-dependent cost. A consideration of  $C(n)$  mandates an evaluation of  $L(n)$ , which is the sample-size-dependent expected financial loss related to the erroneous conclusion that a waste is hazardous. A simple loss function is:

$$L(n) = \frac{\alpha s^2}{n}, \quad (\text{Equation 20})$$

with  $\alpha$  = a constant related to the cost of a waste management program if the waste is judged to be hazardous,  $s^2$  = sample variance, and  $n$  = number of samples. A primary objective of any sampling strategy is to minimize  $C(n) + L(n)$ . Differentiation of Equations 19 and 20 indicates that the number of samples ( $n$ ) which minimize  $C(n) + L(n)$  is:

$$n = \sqrt{\frac{\alpha s^2}{C_1}}. \quad (\text{Equation 21})$$

As is evident from Equation 21, a comparatively large number of samples ( $n$ ) is justified if the value of  $\alpha$  or  $s^2$  is large, whereas a relatively small number of samples is appropriate if the value of  $C_1$  is large. These general conclusions are valid for any sampling strategy for a solid waste.

## 1.2 Implementation of Sampling Plan

This section describes EPA-approved equipment and procedures for obtaining representative samples of a solid waste. The information in this section is general in nature. Since each specific sampling situation is unique, the equipment and procedures described must be modified appropriately in an actual use situation to ensure that representative samples are collected. It is the responsibility of those persons conducting sampling programs to make the appropriate modifications.

### 1.2.1 Selection of Sampling Equipment

Sampling the diverse types of RCRA-regulated wastes requires a variety of different types of samplers. Several sampling devices are described in this section. Some of these samplers are commercially available. Others will have to be fabricated by the user. Table 1 is a general guide to the types of waste that can be sampled by each of the samplers described.

#### 1.2.1.1 Composite Liquid Waste Sampler (Coliwasa)

##### Scope and Purpose

The Coliwasa is a device employed to sample free-flowing liquids and slurries contained in drums, shallow open-top tanks, pits, and similar containers. It is especially useful for sampling wastes that consist of several immiscible liquid phases.

The Coliwasa consists of a glass, plastic, or metal tube equipped with an end closure which can be opened and closed while the tube is submerged in the material to be sampled.

The Coliwasa was developed by the California Department of Health under a grant from the U.S. EPA. A more detailed discussion of the Coliwasa can be found in the Department of Health's report "Samplers and Sampling Procedures for Hazardous Waste Streams," Grant No. R804692010, MERL, USEPA, Cincinnati, Ohio. A modification of the device is described in "Evaluation of the Procedures for Identification of Hazardous Wastes," by L.R. Williams et al. (EPA/EMSC, Las Vegas, Nevada).

It should be mentioned that some experienced sampling personnel find the Coliwasa cumbersome and difficult to clean or dispose of following use.

##### General Comments and Precautions

1. Do not use a plastic Coliwasa, unless it is constructed of fluorocarbons (e.g., Teflon), to sample wastes containing organic materials.

TABLE 1. SAMPLING EQUIPMENT FOR PARTICULAR WASTE TYPES

Waste type	Waste location or container								
	Drum	Sacks and bags	Open bed truck	Closed bed truck	Storage tanks or bins	Waste files	Ponds, lagoons, & pits	Conveyor belt	Pipe
Free flowing liquids and slurries	Coliwasa	N/A	N/A	Coliwasa	Weighted bottle	N/A	Dipper	N/A	Dipper
Sludges	Trier	N/A	Trier	Trier	Trier	a	a		
Moist powders or granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	Dipper
Dry powders or granules	Thief	Thief	Thief	Thief	Thief	Thief	Thief	Shovel	Dipper
Sand or packed powders and granules	Auger	Auger	Auger	Auger	a	a	a	Dipper	Dipper
Large grained solids	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Trier	Dipper

<sup>a</sup>This type of sampling situation can present significant logistical sampling problems, therefore sampling equipment must be specifically selected or designed based on site and waste conditions. No general statement about appropriate sampling equipment can be made.

2. Do not use a glass Coliwasa to sample liquids that contain hydrofluoric acid.
3. If significant amounts of solid material are present within 2 inches of the bottom of the container to be sampled, special procedures will be necessary to obtain a representative sample of this solid phase.

### Apparatus

Coliwesas are available commercially (NASCO) or can be fabricated to conform to the specifications detailed in Figure 1. Table 2 lists the parts required to fabricate a plastic or glass Coliwasa.

### Assembly

Assemble Coliwasa sampler as follows:

1. Attach swivel to the T-handle with the 3.12-cm-long bolt and secure with the 3/16-in. NC washer and lock nut.
2. Shape stopper into a cone by boring a 0.95-cm hole through the center of the stopper. Insert a short piece of 0.95-cm-O.D. handle through the hole until the end of the handle is flush against the bottom (smaller diameter) surface of the stopper. Carefully and uniformly turn the stopper into a cone against a grinding wheel. This is done by turning the stopper with the handle and grinding it down conically from about 0.5 cm of the top (larger diameter) surface to the edge of the 0.95-cm-hole on the bottom surface. Attach neoprene stopper to one end of the stopper rod and secure with the 3.8-in. NC washer and lock nut.
3. Install the stopper and stopper rod assembly in the sampling tube.
4. Secure locking block sleeve on the block with glue or screws.
5. Position the locking block on top of the sampling tube so that the sleeveless portion of the block fits inside the tube, the sleeve sits against the top end of the tube, and the upper end of the stopper rod slips through the center hold of the block.
6. Attach the upper end of the stopper to the swivel of the T-handle.
7. Place the sampler in the closed position and adjust the tension on the stopper by screwing the T-handle in or out.
8. Test the tension by filling the Coliwasa with water to ensure that it is leak free.

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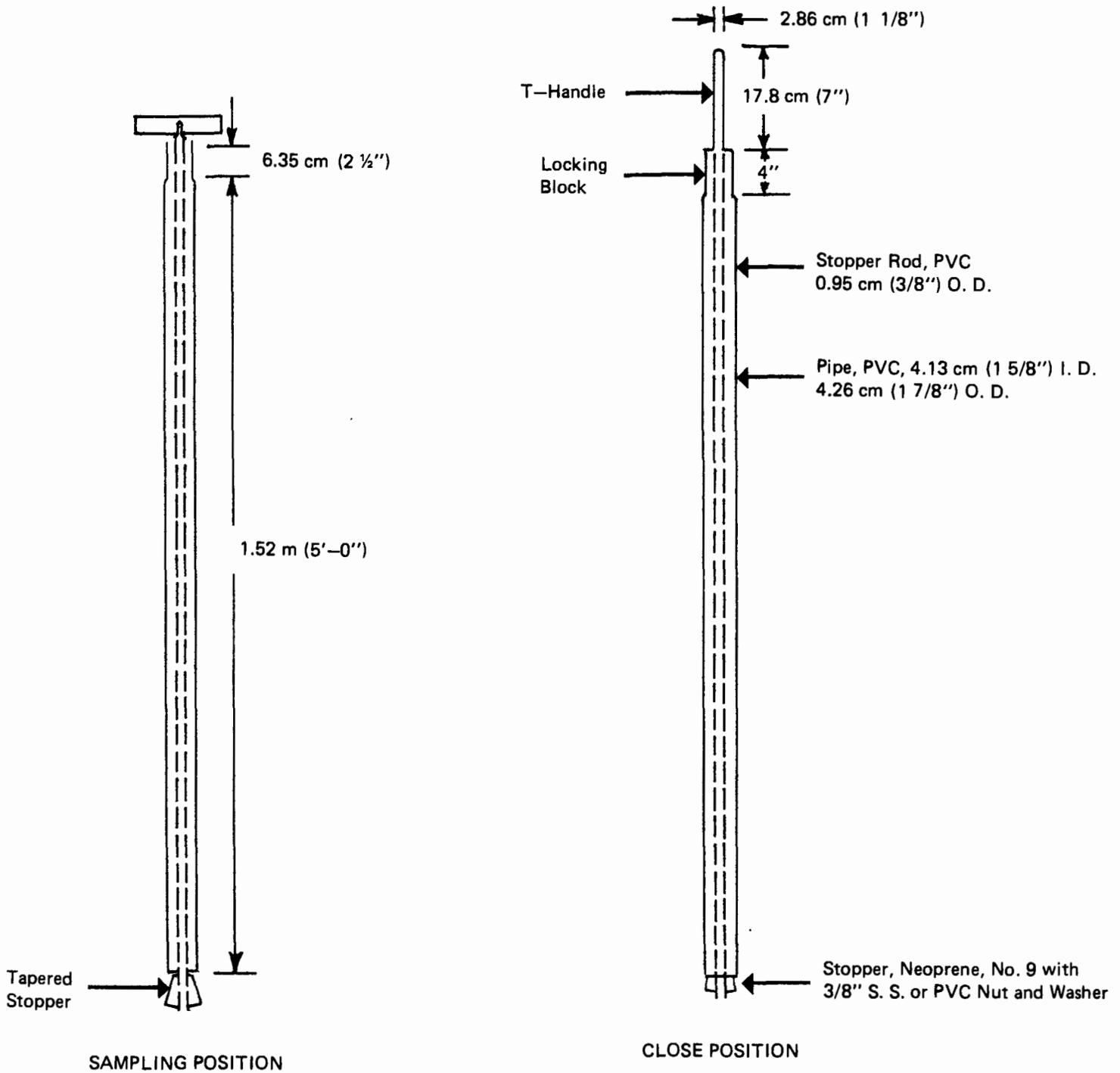


Figure 1. Composite liquid waste sampler (Coliwasa).

TABLE 2. PARTS FOR CONSTRUCTING A COLIWASA

Quantity	Item	Comments	Supplier
1	Sample tube, translucent PVC plastic, 4.13 cm I.D. x 1.52 m long x 0.4 cm wall thickness	Plastic Coliwasa only	Plastic supply houses
1	Sample tube, borosilicate glass, 4.13 cm I.D. x 1.52 m long	Glass Coliwasa only	Corning Glass Works #72-1602
1	Stopper, neoprene rubber #9		Laboratory supply house
1	Stopper rod, PVC, 0.95 cm O.D. x 1.67 m long	Plastic Coliwasa only	Plastic supply houses
1	Stopper rod, teflon, 0.95 cm O.D. x 1.67 m long	Glass or Plastic Coliwasa	Plastic supply houses
1	Locking block, PVC, 3.8 cm O.D. x 10.2 cm long with 0.56-cm hole in center	Fabricate by drilling 0.56-cm hole through center	Plastic supply houses
1	Locking block sleeve, PVC, 4.13 cm I.D. x 6.35 cm long	Fabricate from stock 4.13-cm PVC pipe	Plastic supply houses
1	T-handle, aluminum, 18 cm long x 2.86 cm wide with 1.27-cm-wide channel	Fabricate from aluminum bar stock	Hardware stores
1	Swivel, aluminum bar 1.27 cm square x 5.08 cm long with 3/8-in. NC inside thread to attach stopper rod	Fabricate from aluminum bar stock	Hardware stores

TABLE 2 (CONT.)

Quantity	Item	Comments	Supplier
1	Nut, PVC, 3/8 in. NC		Plastic supplier
1	Washer, PVC, 3/8 in. NC		Plastic supplier
1	Nut, stainless steel, 3/8 in. NC		Hardware stores
1	Washer, stainless steel, 3/8 in.		Hardware stores
1	Bolt, 3.12 cm long x 3.16 in. NC		Hardware stores
1	Nut, 3/16 in. NC		Hardware stores
1	Washer, lock 3/16 in.		Hardware stores

### Procedure

1. Clean Coliwasa.
2. Adjust sampler's locking mechanism to ensure that the stopper provides a tight closure. Open sampler by placing stopper rod handle in the T-position and pushing the rod down until the handle sits against the sampler's locking block.
3. Slowly lower the sampler into the waste at a rate that permits the level of liquid inside and outside the sampler to remain the same. If the level of waste in the sampler tube is lower inside than outside, the sampling rate is too fast and will produce a nonrepresentative sample.
4. When the sampler hits the bottom of the waste container, push sampler tube down to close and lock the stopper by turning the T-handle until it is upright and one end rests on the locking block.
5. Withdraw Coliwasa from waste and wipe the outside with a disposable cloth or rag.

#### 1.2.1.2 Weighted Bottle

##### Scope and Application

This sampler consists of a glass or plastic bottle, sinker, stopper, and a line which is used to lower, raise, and open the bottle. The weighted bottle samples liquids and free-flowing slurries.

##### General Comments and Precautions

1. Do not use a nonfluorocarbon plastic bottle to sample wastes containing organic materials.
2. Do not use a glass bottle to sample wastes that contain hydrofluoric acid.
3. Before sampling, ensure that the waste will not corrode the sinker, bottle holder, or line.

##### Apparatus

A weighted bottle with line is built to the specifications in ASTM Methods D 270 and E 300. Figure 2 shows the configuration of a weighted bottle sampler.

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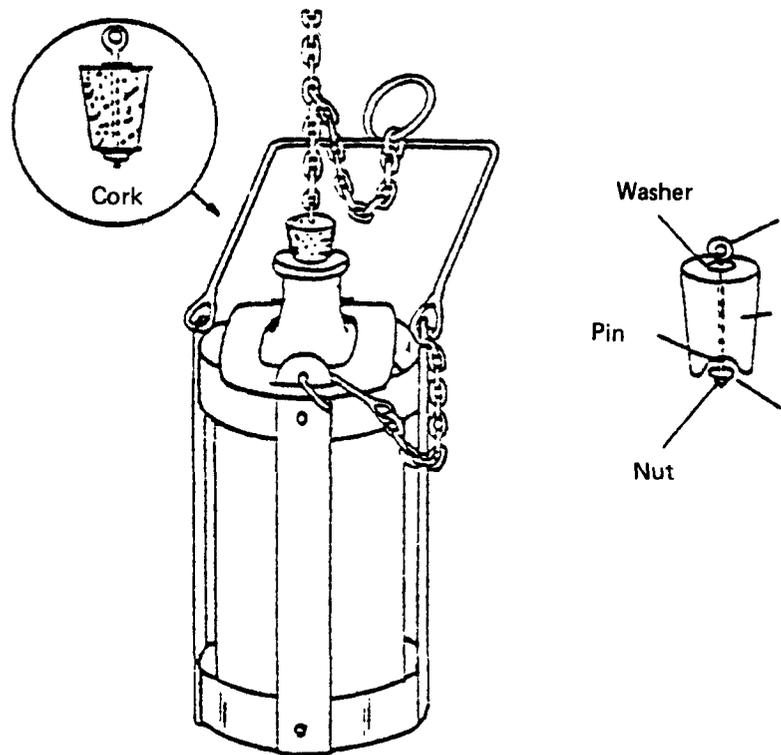


Figure 2. Weighted bottle sampler.

### Procedure

1. Clean bottle.
2. Assemble weighted bottle sampler.
3. Lower the sampler to directed depth and pull out the bottle stopper by jerking the line.
4. Allow bottle to fill completely as evidenced by cessation of air bubbles.
5. Raise sampler, cap, and wipe off with a disposable cloth. The bottle can serve as a sample container.

#### 1.2.1.3 Dipper

### Scope and Application

The dipper consists of a glass or plastic beaker clamped to the end of a 2- or 3-piece telescoping aluminum or fiberglass pole which serves as the handle. A dipper samples liquids and free-flowing slurries.

### General Comments and Precautions

1. Do not use a nonfluorocarbon plastic beaker to sample wastes containing organic materials.
2. Do not use a glass beaker to sample wastes of high pH or wastes that contain hydrofluoric acid.
3. Paint aluminum pole and clamp with a 2-part epoxy or other chemical-resistant paint when sampling either alkaline or acidic wastes.

### Apparatus

Dippers are not available commercially and must be fabricated to conform to the specifications detailed in Figure 3. Table 3 lists the parts required to fabricate a dipper.

### Procedure

1. Clean beaker, clamp, and handle.
2. Assemble dipper by bolting adjustable clamp to the pole. Place beaker in clamp and fasten shut.
3. Turn dipper so the mouth of the beaker faces down and insert into waste material. Turn beaker right side up when dipper is at desired depth. Allow beaker to fill completely as shown by the cessation of air bubbles.
4. Raise dipper and transfer sample to container.

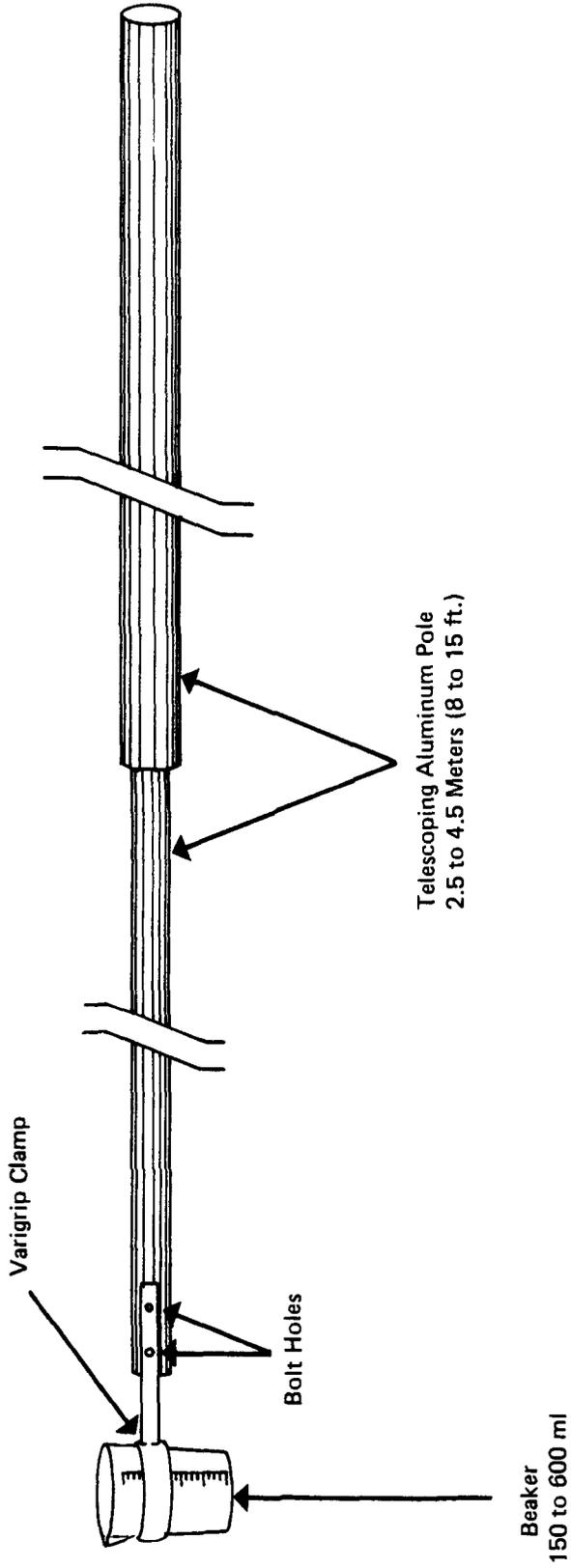


Figure 3. Dipper.

TABLE 3. PARTS FOR CONSTRUCTING A DIPPER

Quantity	Item	Supplier
1	Adjustable clamp, 6.4 to 8.9 cm (2-1/2 to 3-1/2 in.) for 250- to 600-ml beakers. Heavy-duty aluminum	Laboratory supply houses
1	Tube 2.5 to 4.5 m long with joint cam locking mechanism. Diameter 2.54 cm I.D. and 3.18 cm I.D.	Swimming pool supply houses
1	Polypropylene or glass beaker, 250 ml to 600 ml	Laboratory supply houses
4	Bolts 2-1/4 in. x 1/4 in., NC	Hardware stores
4	Nuts, 1/4 in., NC	Hardware stores

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### 1.2.1.4 Thief

#### Scope and Application

A thief consists of two slotted concentric tubes usually made of stainless steel or brass. The outer tube has a conical pointed tip which permits the sampler to penetrate the material being sampled. The inner tube is rotated to open and close the sampler. A thief is used to sample dry granules or powdered wastes whose particle diameter is less than one-third the width of the slots.

#### Apparatus

A thief is available at laboratory supply stores (Figure 4).

#### Procedure

1. Clean sampler.
2. Insert closed thief into waste material. Rotate inner tube to open thief. Wiggle the unit to encourage material to flow into thief. Close thief and withdraw. Place sampler thief in a horizontal position with the slots facing upward. Remove inner tube from thief and transfer sample to a container.

### 1.2.1.5 Trier

#### Scope and Application

A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and loosen soil. A trier samples moist or sticky solids with a particle diameter less than one-half the diameter of the trier.

#### Apparatus

1. Triers 61 to 100 cm long and 1.27 to 2.54 cm in diameter are available at laboratory supply stores.
2. A large trier can be fabricated to conform to the specifications in Figure 5. A metal or polyvinyl chloride pipe, 1.52 m (5 ft) long x 3.2 cm (1.4 in.) I.D., with a 0.32-cm (1-1/8 in.) wall thickness, is needed. The pipe should be sawed lengthwise, about 60-40 split, to form a trough stretching from one end to 10 cm away from the other end. The edges of the slot and the tip of the pipe are sharpened to permit the sampler to cut into the waste material being sampled. The unsplit length of the pipe serves as the handle.

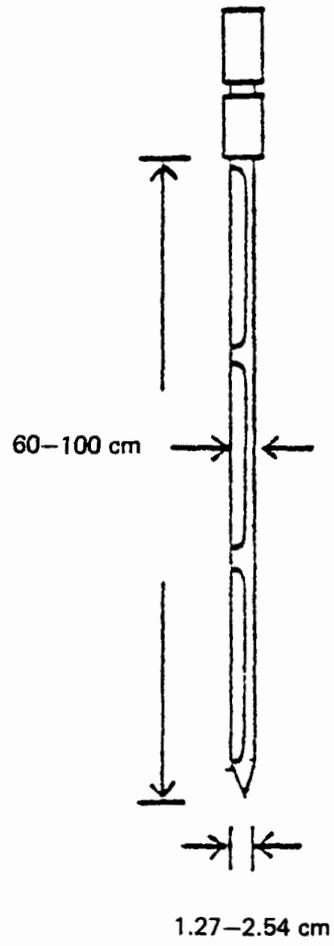


Figure 4. Thief sampler.

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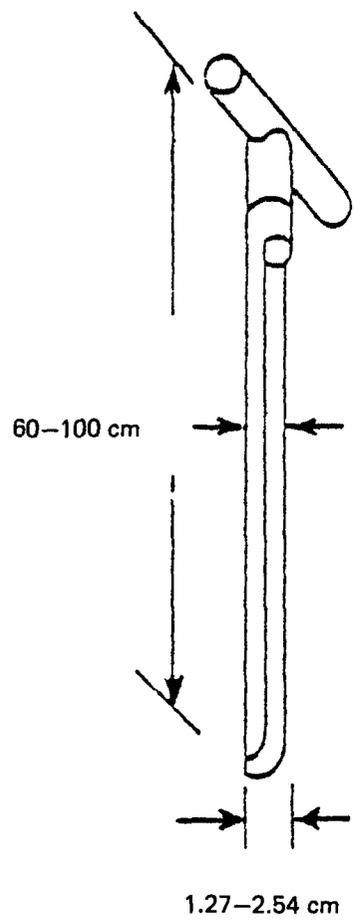
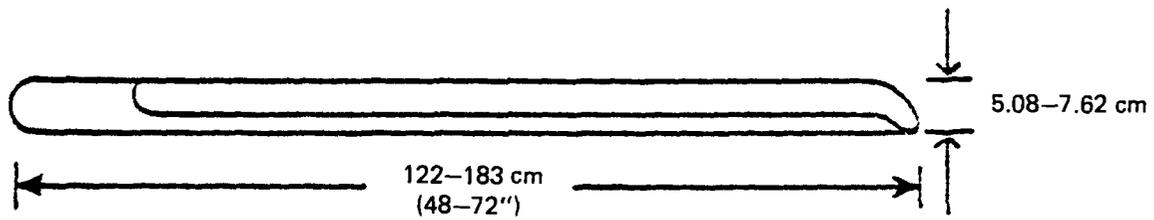


Figure 5. Sampling triers.

Procedure

1. Clean trier.
2. Insert trier into waste material 0 to 45° from horizontal. Rotate trier to cut a core of the waste. Remove trier with concave side up and transfer sample to container.

1.2.1.6 Auger

Scope and Application

An auger consists of sharpened spiral blades attached to a hard metal central shaft. An auger samples hard or packed solid wastes or soil.

Apparatus

Augers are available at hardware and laboratory supply stores.

Procedure

1. Clean sampler.
2. Bore a hole through the middle of an aluminum pie pan large enough to allow the blade of the auger to pass through. The pan will be used to catch the sample brought to the surface by the auger.
3. Place pan against the sampling point. Auger through the hole in the pan until the desired sampling depth is reached. Back off the auger and transfer the sample in the pan and adhering to the auger to a container. Spoon out the rest of the loosened sample with a sample trier.

1.2.1.7 Scoop and Shovel

Scope and Application

Scoops and shovels are used to sample granular or powdered material in bins, shallow containers and conveyor belts.

Apparatus

Scoops are available at laboratory supply houses. Flat-nosed shovels are available at hardware stores.

Procedure

1. Clean sampler.
2. Obtain a full cross section of the waste material using a scoop or shovel that is large enough to contain the waste collected in one cross section sweep.

1.2.2 Selection of Sample Containers

The most important factors to consider when choosing containers for hazardous waste samples are compatibility with the waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with constituents of waste samples. Thus, it is important to have some idea of the properties and composition of the waste. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are desirable to facilitate transfer of samples from samplers to containers. Also, the containers must be large enough to contain the optimum sample volume.

Containers for collecting and storing hazardous waste samples are usually made of plastic or glass. Plastics that are commonly used to make the containers include high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, teflon FEP (fluorinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is almost universally usable due to its chemical inertness and resistance to breakage. However, its high cost severely limits its use. LPE, on the other hand, usually offers the best combination of chemical resistance and low cost when samples are to be analyzed for inorganic parameters.

Glass containers are relatively inert to most chemicals and can be used to collect and store almost all hazardous waste samples except those that contain strong alkali and hydrofluoric acid. Soda glass bottles are suggested due to their low cost and ready availability. Borosilicate glass containers, such as Pyrex and Corex, are more inert and more resistant to breakage than soda glass but are expensive and not always readily available. Glass containers are generally more fragile and much heavier than plastic containers. Glass or FEP containers must be used for waste samples that will be analyzed for organic compounds.

The containers must have tight, screw-type lids. Plastic bottles are usually provided with screw caps made of the same material as the bottles. Buttress threads are recommended. Cap liners are not usually required for plastic containers. Teflon cap liners should be used with glass containers supplied with rigid plastic screw caps. Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Maryland 21133). These caps are usually provided with waxed paper liners. Other liners that may be suitable are polyethylene, polypropylene, and neoprene plastics.

### 1.2.3 Processing and Storage of Samples

Once a sample has been collected, steps must be taken to preserve the chemical and physical integrity of the sample during transport and storage prior to analysis. The type of sample preservation required will vary according to the sample type and the parameter to be measured.

Preservation and storage requirements are described in the individual analytical methods in this manual. Since these requirements vary with the analytical method to be employed, it may be necessary to prepare more than one container of the same waste if more than one type of analysis is to be conducted. The chemical makeup of the samples can alter the effectiveness of preservation, therefore all sample analyses should be performed as soon as possible after sampling.

Section 1.3 of this manual describes specifications for packaging and shipping samples.

## SAMPLING - Implementation; Chain of Custody

### 1.3 Documentation of Chain of Custody

An essential part of any sampling/analytical scheme is ensuring the integrity of the sample from collection to data reporting. This includes the ability to trace the possession and handling of samples from the time of collection through analysis and final disposition. This documentation of the history of the sample is referred to as Chain of Custody.

Chain of custody is necessary if there is any possibility that the analytical data or conclusions based upon analytical data will be used in litigation. In cases where litigation is not involved, many of the chain-of-custody procedures are still useful for routine control of sample flow. The components of chain of custody - sample seals, a field log book, chain-of-custody record, and sample analysis request sheet - and the procedures for their use are described in the following sections.

A sample is considered to be under a person's custody if (1) it is in a person's physical possession, (2) in view of the person after he has taken possession, (3) secured by that person so that no one can tamper with the sample, or (4) secured by that person in an area which is restricted to authorized personnel. A person who has samples under his custody must comply with the procedures described in the following sections.

The material presented here briefly summarizes the major aspects of chain of custody. The reader is referred to NEIC Policies and Procedures, EPA-330/9/78/001-R (as revised 1/82), or other manual as appropriate, for more information.

#### 1.3.1 Sample Labels

Sample labels (Figure 1) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate and should include at least the following information:

- Sample number
- Name of collector
- Date and time of collection
- Place of collection

Labels should be affixed to sample containers prior to or at the time of sampling. The labels should be filled out at the time of collection.

#### 1.3.2 Sample Seals

Sample seals are used to detect unauthorized tampering of samples following sample collection up to the time of analysis. Gummed paper seals may be used for this purpose. The paper seal should include, at least, the following information:

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Collector \_\_\_\_\_ Sample No. \_\_\_\_\_

Place of Collection \_\_\_\_\_

---

Date Sampled \_\_\_\_\_ Time Sampled \_\_\_\_\_

Field Information \_\_\_\_\_

---

---

Figure 1. Example of Sample Label

Sample number (This number must be identical with the number on the sample label)

Collector's name

Date and time of sampling

The seal must be attached in such a way that it is necessary to break it in order to open the sample container. An example of a sample seal is shown in Figure 2. Seals must be affixed to containers before the samples leave the custody of sampling personnel.

### 1.3.3 Field Log Book

All information pertinent to a field survey or sampling must be recorded in a log book. This should be bound, preferably with consecutively numbered pages that are 21.6 by 27.9 cm (8-1/2 by 11 in.). As a minimum, entries in the log book must include the following:

Purpose of sampling (e.g., surveillance, contract number)

Location of sampling point

Name and address of field contact

Producer of waste and address, if different than location

Type of process (if known) producing waste

Type of waste (e.g., sludge, wastewater)

Suspected waste composition, including concentrations

Number and volume of sample taken

Description of sampling point and sampling methodology

Date and time of collection

Collector's sample identification number(s)

Sample distribution and how transported (e.g., name of laboratory, UPS, Federal Express)

References such as maps or photographs of the sampling site

Field observations

Any field measurements made (e.g., pH, flammability, explosivity)

Signatures of personnel responsible for observations



Sampling situations vary widely. No general rule can be given as to the extent of information that must be entered in the log book. A good rule, however, is to record sufficient information so that someone can reconstruct the sampling without reliance on the collector's memory.

The log book must be protected and kept in a safe place.

#### 1.3.4 Chain-of-Custody Record

To establish the documentation necessary to trace sample possession from the time of collection, a chain-of-custody record should be filled out and accompany every sample. This record becomes especially important if the sample is to be introduced as evidence in a court litigation. A chain-of-custody record is illustrated in Figure 3.

The record should contain the following minimum information.

Sample number

Signature of collector

Date and time of collection

Place and address of collection

Waste type

Signature of persons involved in the chain of possession

Inclusive dates of possession

#### 1.3.5 Sample Analysis Request Sheet

The sample analysis request sheet (Figure 4) is intended to accompany the sample on delivery to the laboratory. The field portion of this form is completed by the person collecting the sample and should include most of the pertinent information noted in the log book. The laboratory portion of this form is intended to be completed by laboratory personnel and to include at a minimum:

Name of person receiving the sample

Laboratory sample number

Date of sample receipt

Sample allocation

Analyses to be performed



## SAMPLING ANALYSIS REQUEST

## PART I: Field Section

Collector \_\_\_\_\_ Date Sampled \_\_\_\_\_ Time \_\_\_\_\_ hours

Affiliation of Sampler \_\_\_\_\_

Address \_\_\_\_\_  
number street city state zip

Telephone (\_\_\_\_) \_\_\_\_\_ Company Contact \_\_\_\_\_

## LABORATORY

LABORATORY SAMPLE NUMBER	COLLECTOR'S SAMPLE NO.	TYPE OF SAMPLE*	FIELD INFORMATION**
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Analysis Requested \_\_\_\_\_

Special Handling and/or Storage \_\_\_\_\_

## PART II: LABORATORY SECTION\*\*

Received by \_\_\_\_\_ Title \_\_\_\_\_ Date \_\_\_\_\_

Analysis Required \_\_\_\_\_

\* Indicate whether sample is soil, sludge, etc.

\*\*Use back of page for additional information relative to sample location.

Figure 4. Example of hazardous waste sample analysis request sheet.

### 1.3.6 Sample Delivery to the Laboratory

The sample should be delivered to the laboratory for analysis as soon as practicable - usually within 1 or 2 days after sampling. The sample must be accompanied by the chain-of-custody record (Figure 3) and by a sample analysis request sheet (Figure 4). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

### 1.3.7 Shipping of Samples

Any material that is identified in the DOT Hazardous Material Table (49 CFR 172.101) must be transported as prescribed in the table. All other hazardous waste samples must be transported as follows:

1. Collect sample in a 16-ounce or smaller glass or polyethylene container with nonmetallic teflon-lined screw cap. Allow sufficient air space (approximately 10% by volume) so container is not liquid full at 54° C (130° F). If collecting a solid material, the container plus contents should not exceed 1 pound net weight. If sampling for volatile organic analysis, fill VOA container to septum but place the VOA container inside a 16-ounce or smaller container so the required air space may be provided. Large quantities, up to 3.785 liters (1 gallon), may be collected if the sample's flash point is 23° C (75° F) or higher. In this case, the flash point must be marked on the outside container (e.g., carton, cooler), and shipping papers should state that "Flash point is 73° F or higher."
2. Seal sample and place in a 4-mil-thick polyethylene bag, one sample per bag.
3. Place sealed bag inside a metal can with noncombustible, absorbent cushioning material (e.g., vermiculite or earth) to prevent breakage, one bag per can. Pressure-close the can and use clips, tape or other positive means to hold the lid securely.
4. Mark the can with:

Name and address of originator  
"Flammable Liquid N.O.S. UN 1993"  
(or "Flammable Solid N.O.S. UN 1325")

NOTE: UN numbers are now required in proper shipping names.

5. Place one or more metal cans in a strong outside container such as a picnic cooler or fiberboard box. Preservatives are not used for hazardous waste site samples.

6. Prepare for shipping:

"Flammable Liquid, N.O.S. UN 1993" or "Flammable Solid, N.O.S. UN 1325"; "Cargo Aircraft Only" (if more than 1 quart net per outside package); "Limited Quantity" or "Ltd. Qty."; "Laboratory Samples"; "Net Weight \_\_\_" or "Net Volume \_\_\_" (of hazardous contents) should be indicated on shipping papers and on outside of outside shipping container. "This Side Up" or "This End Up" should also be on container. Sign shipper certification.

7. Stand by for possible carrier requests to open outside containers for inspection or modify packaging. It is wise to contact carrier before packing to ascertain local packaging requirements and not to leave area before the carrier vehicle (aircraft, truck, etc.) is on its way.

1.3.8 Receipt and Logging of Sample

In the laboratory, a sample custodian should be assigned to receive the samples. Upon receipt of a sample, the custodian should inspect the condition of the sample and the sample seal, reconcile the information on the sample label and seal against that on the chain-of-custody record, assign a laboratory number, log in the sample in the laboratory log book, and store the sample in a secured sample storage room or cabinet until assigned to an analyst for analysis.

The sample custodian should inspect the sample for any leakage from the container. A leaky container containing multiphase sample should not be accepted for analysis. This sample will no longer be a representative sample. If the sample is contained in a plastic bottle and the container walls show that the sample is under pressure or releasing gases, the sample should be treated with caution since it may be explosive or release extremely poisonous gases. The custodian should examine whether the sample seal is intact or broken, since a broken seal may mean sample tampering and would make analysis results inadmissible in court as evidence. Any discrepancies between the information on the sample label and seal and the information that is on the chain-of-custody record and the sample analysis request sheet should be resolved before the sample is assigned for analysis. This effort might require communication with the sample collector. Results of the inspection should be noted on the sample analysis request sheet and on the laboratory sample log book.

Incoming samples usually carry the inspector's or collector's identification numbers. To further identify these samples, the laboratory should assign its own identification numbers, which normally are given consecutively. Each sample should be marked with the assigned laboratory number. This number is correspondingly recorded on a laboratory sample log book along with the information describing the sample. The sample information is copied from the sample analysis request sheet and cross-checked against that on the sample label.

### 1.3.9 Assignment of Sample for Analysis

In most cases, the laboratory supervisor assigns the sample for analysis. The supervisor should review the information on the sample analysis request sheet, which now includes inspection notes recorded by the laboratory sample custodian. The technician assigned to analysis should record in the laboratory notebook the identifying information about the sample, the date of receipt, and other pertinent information. This record should also include the subsequent testing data and calculations. The sample may have to be split with other laboratories in order to obtain all the necessary analytical information. In this case, the same type of chain-of-custody procedures must be employed at the other laboratory and while the sample is being transported to the other laboratory.

Once the sample has been received in the laboratory, the supervisor or his assignee is responsible for its care and custody. He should be prepared to testify that the sample was in his possession or secured in the laboratory at all times from the moment it was received from the custodian until the analyses were performed.

## 1.4 Sampling Methodology

The sampling methodology will be determined in part by the sampling strategy to be employed. Four different types of sampling strategies (simple random, stratified random, systematic random, and authoritative sampling) were discussed in Section 1.1. The latter three strategies require more information than the simple random approach. This additional information must either be acquired through sampling or must be estimated. The information requirements of the sampling strategy to be used should be kept in mind when designing a sampling plan.

The methods and equipment used for sampling waste materials will vary with the form and consistency of the waste materials to be sampled. Samples collected using the sampling protocols listed below, for sampling waste with properties similar to the indicated materials, will be considered by the Agency to be representative of the waste.

Extremely viscous liquid	ASTM Standard D140-70 <sup>1</sup>
Crushed or powdered material	ASTM Standard D346-75
Soil or rock-like material	ASTM Standard D420-69
Soil-like material	ASTM Standard D1452-65
Fly-ash-like material	ASTM Standard D2234-76

### 1.4.1 Containers

The term container as used here refers to receptacles that are designed for transporting materials, e.g., drums and other smaller receptacles as opposed to stationary tanks. (Stationary tanks are discussed in Section 1.4.2.) Weighted bottles, Coliwasas, drum thieves, or triers are the sampling devices which are chosen for the sampling of containers.

The sampling strategy for containers varies according to (1) the number of containers to be sampled, and (2) access to the containers. Ideally, if the waste is contained in several containers, every container will be sampled. If this is not possible due to the large number of containers or cost factors, a subset of individual containers must be randomly selected for sampling. This can be done by assigning each container a number and then randomly choosing a set of numbers for sampling.

Access to a container will affect the number of samples that can be taken from the container and the location within the container from which samples can be taken. Ideally, several samples should be taken from locations displaced both vertically and horizontally throughout the waste. The number of samples required for reliable sampling will vary depending on the distribution of the waste components in the container. As a minimum with an unknown waste, a sufficient number and distribution of samples should be taken to address any possible vertical anomalies in the

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<sup>1</sup>ASTM Standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.

## 2 / SAMPLING - Methodology

waste. This is because contained wastes have a much greater tendency to be nonrandomly heterogeneous in a vertical rather than a horizontal direction due to (1) settling of solids and the denser phases of liquids, and (2) variation in the content of the waste as it entered the container. Bags, paper drums, and open-headed steel drums (of which the entire top can be removed) generally do not restrict access to the waste and therefore do not limit sampling.

When access to a container is unlimited, a useful strategy for obtaining a representative set of samples is a three-dimensional simple random sampling strategy in which the container is divided by constructing an imaginary three-dimensional grid (see Figure 1). This is done as follows. First, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the container is large. (Cylindrical containers can be divided into imaginary concentric circles which are then further divided into grids of equal size.) Each section is assigned a number. The height of the container is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are then assigned numbers. Specific levels and grid locations are then selected for sampling using a random number table or random number generator.

Another appropriate sampling approach is the two-dimensional simple random sampling strategy, which can usually yield a more precise sampling when fewer samples are collected. This strategy involves (1) dividing the top surface of the waste into an imaginary grid as in the three-dimensional strategy, (2) selecting grid sections for sampling using random number tables or number generators, and (3) sampling each selected grid point in a vertical manner along the entire length from top to bottom using a sampling device such as a drum thief, or Coliwasa.

Some containers such as drums with bung openings limit access to the contained waste and restrict sampling to a single vertical plane. Samples taken in this manner can be considered representative of the entire container only if the waste is known to be homogeneous. Precautions must be taken when sampling any type of steel drum since the drum may explode or expel gases and/or pressurized liquids. An EPA/NEIC manual, "Safety Manual for Hazardous Waste Site Investigation," addresses these safety precautions.

### 1.4.2 Tanks

Tanks are essentially large containers. The considerations involved in sampling tanks are therefore similar to those for sampling containers (Section 1.4.1). As with containers, the goal of sampling tanks is to acquire a sufficient number of samples from different locations within the waste to provide analytical data that are representative of the entire tank contents. The accessibility of the tank contents will affect the sampling methodology.

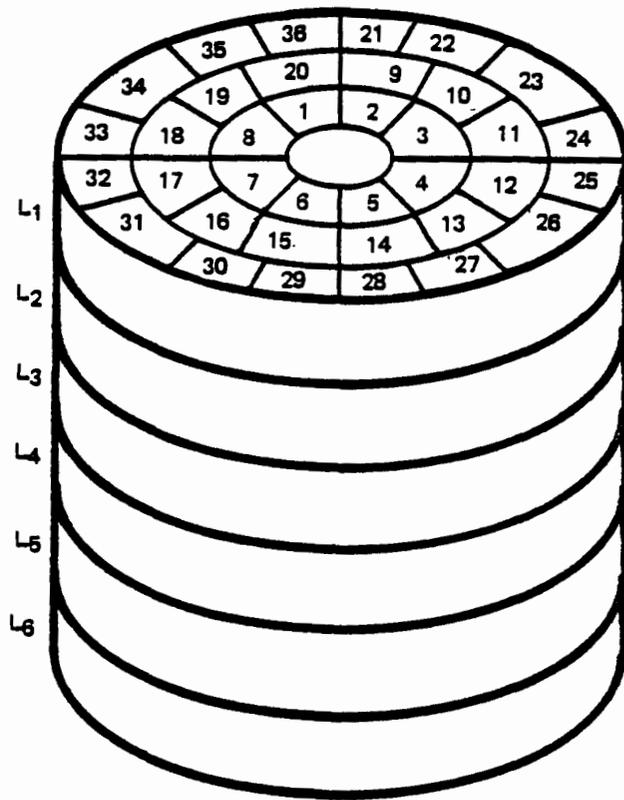


Figure 1. Container divided into an imaginary three-dimensional grid.

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If the tank is an open one, allowing unrestricted access, then usually a representative set of samples is best obtained using the three-dimensional simple random sampling strategy described in Section 1.4.1. This strategy involves dividing the tank contents into an imaginary three-dimensional grid. As a first step, the top surface of the waste is divided into a grid whose sections either approximate the size of the sampling device or are larger than the sampling device if the tank is large. (Cylindrical tanks can be divided into imaginary concentric circles which are then further divided into grids of equal size.) Each section is assigned a number. The height of the tank is then divided into imaginary levels that are at least as large as the vertical space required by the chosen sampling device. These imaginary levels are assigned numbers. Specific levels and grid locations are then selected for sampling using a random number table or random number generator.

A less comprehensive sampling approach may be appropriate if information regarding the distribution of waste components is known or assumed (e.g., vertical compositing will yield a representative sample). In such cases, a two-dimensional simple random sampling strategy may be appropriate. In this strategy, the top surface of the waste is divided into an imaginary grid; grid sections are selected using random number tables or number generators; and each selected grid point is then sampled in a vertical manner along the entire length from top to bottom using a sampling device such as a weighted bottle, a drum thief, or Coliwasa. If the waste is known to consist of two or more discrete strata, a more precise representation of the tank contents can be obtained by using a stratified random sampling strategy, i.e., sampling each stratum separately using the two- or three-dimensional simple random sampling strategy.

Some tanks permit only limited access to their contents, which restricts the locations within the tank from which samples can be taken. If sampling is restricted, the sampling strategy must, as a minimum, take sufficient samples to address the potential vertical anomalies in the waste in order to be considered representative. This is because contained wastes tend to display vertical, rather than horizontal, nonrandom heterogeneity due to settling of suspended solids or denser liquid phases. If access restricts sampling to a portion of the tank contents (e.g., in an open tank, the size of the tank may restrict sampling to the perimeter of the tank; in a closed tank, the only access to the waste may be through inspection ports), then the resulting analytical data will only be deemed representative of the accessed area, not of the entire tank contents unless the tank contents are known to be homogeneous.

If a limited access tank is to be sampled, and little is known about the distribution of components within the waste, a set of samples that are representative of the entire tank contents can be obtained by taking a series of samples as the tank contents are being drained. This should be done in a simple random manner by estimating how long it will take to drain the tank and then randomly selecting times during drainage for sampling.

The most appropriate type of sampling device for tanks depends on the tank parameters. In general, shallow tanks are sampled using subsurface samplers (i.e., pond samplers), while weighted bottles are usually employed for tanks deeper than 5 ft. Dippers are useful for sampling pipe effluents.

#### 1.4.3 Waste Piles

Waste accessibility, which is frequently a function of pile size, is a key factor in the design of a sampling strategy for a waste pile. Ideally, piles containing unknown wastes should be sampled using a three-dimensional simple random sampling strategy. This strategy can be employed only if all points within the pile can be accessed. In such cases, the pile should be divided into a three-dimensional grid system, the grid sections assigned numbers, and the sampling points then chosen using random number tables or number generators.

If sampling is limited to certain portions of the pile, then the collected sample will be representative only of those portions unless the waste is known to be homogeneous.

In cases where the size of a pile impedes access to the waste, a set of samples that are representative of the entire pile can be obtained with a minimum of effort by scheduling sampling to coincide with pile removal. The number of truckloads needed to remove the pile should be estimated, and the truckloads randomly chosen for sampling.

The sampling devices most commonly used for small piles are thieves, triers, and shovels. Excavation equipment such as backhoes can be useful for sampling medium-sized piles.

#### 1.4.4 Landfills and Lagoons

Landfills contain primarily solid waste, while lagooned waste may range from liquids to dried sludge residues. Lagooned waste that is either liquid or semisolid is often best sampled using the methods recommended for large tanks (see Section 1.4.2). Usually solid wastes contained in a landfill or lagoon are best sampled using the three-dimensional random sampling strategy.

The three-dimensional random sampling strategy involves establishing an imaginary three-dimensional grid of sampling points in the waste and then using random number tables or generators to select points for sampling. In the case of landfills and lagoons, the grid is established using a survey or map of the area. The map is divided into two two-dimensional grids with sections of equal size. These sections are then assigned numbers sequentially.

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Next, the depth to which sampling will take place is determined and subdivided into equal levels which are also sequentially numbered. (The lowest sampling depth will vary from landfill to landfill. Usually, sampling extends to the interface of the fill and the natural soils. If soil contamination is suspected, sampling may extend into the natural soil.) The horizontal and vertical sampling coordinates are then selected using random number tables or generators. If some information is known about the nature of the waste, then a modified three-dimensional strategy may be more appropriate. For example, if the landfill consists of several cells, a more precise measurement may be obtained by considering each cell as a stratum and employing a stratified three-dimensional random sampling strategy (see Section 1.1).

Hollow stem augers combined with split-spoon samplers are frequently appropriate for sampling landfills. Water-driven or water-rinsed coring equipment should not be used for sampling since the water can rinse chemical components from the sample. Excavation equipment such as backhoes may be useful in obtaining samples at various depths; the resulting holes may be useful for viewing and recording the contents of the landfill.

## SECTION TWO

### WASTE EVALUATION PROCEDURES

#### 2.1 Characteristics of Hazardous Waste

Section 262.11 of the Resource Conservation and Recovery Act regulations requires that a generator of a "solid waste" - i.e., any garbage, refuse, sludge or any other waste that is not excluded under Section 261.4(a) - must:

1. Determine if his waste is excluded.
2. If it is not excluded he must determine if his waste is listed as a hazardous waste.
3. If the waste is not excluded and not listed, then he must evaluate his waste in terms of the four Hazardous Characteristics: Ignitability, Corrosivity, Reactivity, and EP Toxicity, unless he can properly evaluate the waste based upon his own knowledge of the waste (e.g., corrosivity testing may not be required if the generator has a long history of running the waste through steel pipes without any evidence of corrosion).

## 2.1.1 Ignitability

### Introduction

This section discusses the hazardous characteristics of ignitability. The regulatory background of this characteristic is summarized and the regulatory definition of Ignitability is presented. Two testing methods are described in Methods 1010 and 1020.

The objective of the ignitability characteristic is to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started.

### Regulatory Definition

The following definitions have been taken verbatim from the RCRA regulations (40 CFR 261.21).

#### Characteristics of Ignitability Regulation

A solid waste exhibits the characteristic of ignitability if a representative sample of the waste has any of the following properties:

1. It is a liquid, other than an aqueous solution, containing less than 24% alcohol by volume, and has a flash point less than 60° C (140° F), as determined by a Pensky-Martens Closed Cup Tester, using the test method specified in ASTM Standard D-93-79 or D-93-80,<sup>1</sup> or a Setaflash Closed Cup Tester, using the test method specified in ASTM standard D-3278-78,<sup>1</sup> or as determined by an equivalent test method approved by the Administrator under the procedures set forth in §§260.20 and 260.21.
2. It is not a liquid and is capable, under standard temperature and pressure, of causing fire through friction, absorption or moisture, or spontaneous chemical changes and, when ignited, burns so vigorously and persistently that it creates a hazard.
3. It is an ignitable compressed gas as defined in 49 CFR 173.300 and as determined by the test methods described in that regulation or equivalent test methods approved by the Administrator under §§260.20 and 260.21.
4. It is an oxidizer as defined in 49 CFR 173.151.

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<sup>1</sup>ASTM Standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.

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A solid waste that exhibits the characteristic of ignitability, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D001.

### Ignitable Compressed Gas

For the purpose of this regulation the following terminology is defined:

1. Compressed gas. The term "compressed gas" shall designate any material or mixture having in the container an absolute pressure exceeding 40 psi at 21° C (70° F) or, regardless of the pressure at 21° C (70° F), having an absolute pressure exceeding 104 psi at 54° C (130° F), or any liquid flammable material having a vapor pressure exceeding 40 psi absolute at 38° C (100° F) as determined by ASTM Test D-323.
2. Ignitable compressed gas. Any compressed gas as defined in paragraph (a) of this section shall be classed as an "ignitable compressed gas" if any one of the following occurs:
  - a. Either a mixture of 13% or less (by volume) with air forms a flammable mixture or the flammable range with air is wider than 12% regardless of the lower limit. These limits shall be determined at atmospheric temperature and pressure. The method of sampling and test procedure shall be acceptable to the Bureau of Explosives.
  - b. Using the Bureau of Explosives' Flame Projection Apparatus (see Note 1), the flame projects more than 18 inches beyond the ignition source with valve opened fully, or, the flame flashes back and burns at the valve with any degree of valve opening.
  - c. Using the Bureau of Explosives' Open Drum Apparatus (see Note 1), there is any significant propagation of flame away from the ignition source.
  - d. Using the Bureau of Explosives' Closed Drum Apparatus (see Note 1), there is any explosion of the vapor-air mixture in the drum.

NOTE 1: A description of the Bureau of Explosives' Flame Projection Apparatus, Open Drum Apparatus, Closed Drum Apparatus, and method of tests may be procured from the Bureau of Explosives (Association of American Railroads, Operations and Maintenance Dept., Bureau of Explosives, American Railroad Building, Washington, D.C. 20036; 202-293-4048).

Oxidizer

For the purpose of this regulation, an oxidizer is any material that yields oxygen readily to stimulate the combustion of organic matter (e.g., chlorate, permanganate, inorganic peroxide, or a nitrate).

## METHOD 1010<sup>1</sup>

### PENSKY-MARTENS CLOSED-CUP METHOD

#### 1.0 Scope and Application

1.1 Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of fuel oils, lube oils, suspensions of solids, liquids that tend to form a surface film under test conditions, and other liquids.

#### 2.0 Summary of Method

2.1 The sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

#### 3.0 Interferences

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flash point values.

#### 4.0 Apparatus

4.1 Pensky-Martens Closed Flash Tester, as described in Annex A1 of ASTM Method D93-77. (Automatic flash point testers are available and may be advantageous since they save testing time, permit the use of smaller samples, and exhibit other advantages. If automatic testers are used, the user must be sure to follow all the manufacturer's instructions for calibrating, adjusting, and operating the instrument. In any cases of dispute, the flash point as determined manually shall be considered the referee test.)

4.2 Thermometers: Two standard thermometers shall be used with the ASTM Pensky-Martens tester.

4.2.1 For tests in which the indicated reading falls within  $-7^{\circ}$  to  $+110^{\circ}$  C ( $20^{\circ}$  to  $230^{\circ}$  F), inclusive: either (1) an ASTM Pensky-Martens Low Range or Tag Closed Tester Thermometer having a range from  $-7^{\circ}$  to  $+110^{\circ}$  C ( $20^{\circ}$  to  $230^{\circ}$  F) and conforming to the requirements for Thermometers 9C (9F) and as prescribed in ASTM Specification E1, or (2) an IP Thermometer 15C (15F) conforming to specifications given in Annex A3 of ASTM D93-77.

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<sup>1</sup>This method is based on ASTM Method D93-77. Refer to D93-77 or D93-80 for more information.

## 2 / CHARACTERISTICS - Ignitability

4.2.2 For tests in which the indicated reading falls within 110° to 370° C (230° to 700° F): either (1) an ASTM Pensky-Martens High Range Thermometer having a range from 90° to 370° C (200° to 700° F) and conforming to the requirements for Thermometers 10C (10F) as prescribed in Specification E1, or (2) IP Thermometer 16C (16F) conforming to specifications given in Annex A3 of ASTM D93-77.

### 5.0 Reagents

5.1 Calcium chloride.

5.2 p-Xylene reference standard.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples shall not be stored in plastic bottles since volatile materials may diffuse through the walls of the bottle.

### 7.0 Procedure

7.1 Preparation of samples: Samples that do not contain volatile contaminants shall be prepared in the following manner. NOTE: If the sample is suspected of containing volatile contaminants, the treatment described in 7.1.1 and 7.1.2 should be omitted.

7.1.1 Samples of very viscous materials may be warmed until they are reasonably fluid before they are tested. However, no sample should be heated more than is absolutely necessary, and no sample should ever be heated to a temperature that exceeds 17° C (30° F) below the sample's expected flash point.

7.1.2 Samples containing dissolved or free water may be dehydrated with calcium chloride or by filtering through a qualitative filter paper or a loose plug or dry absorbent cotton. Warming the sample is permitted, but it shall not be heated for prolonged periods or above a temperature of 17° C (30° F) below the sample's expected flash point.

#### 7.2 Routine procedure

7.2.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test. Be sure to remove any solvent that was used to clean the apparatus. Fill the cup with the sample to

be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Be sure to properly engage the locating or locking device. Insert the thermometer. Light the test flame and adjust it to a diameter of 5/32 in. (4 mm). Supply the heat at such a rate that the temperature as indicated by the thermometer increases 5° to 6° C (9° to 11° F)/min. Turn the stirrer 90 to 120 rpm, stirring in a downward direction.

7.2.2 If the sample is expected to have a flash point of 110° C (230° F) or below, apply the test flame when the temperature of the sample is from 17° C (30° F) to 28° C (50° F) below the expected flash point and thereafter at a temperature reading that is a multiple of 1° C (2° F). Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 sec, left in its lowered position for 1 sec, and quickly raised to its high position. Do not stir the sample while applying the test flame.

7.2.3 If the sample is expected to have a flash point above 110° C (230° F), apply the test flame in the manner just described at each temperature that is a multiple of 2° C (5° F), beginning at a temperature of 17° C (30° F) to 28° C (50° F) below the expected flash point.

NOTE: When testing materials to determine if volatile contaminants are present, it is not necessary to adhere to the temperature limits for initial flame application as stated in 7.2.2 and 7.2.3.

7.2.4 Record as the flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash. The actual flash will have occurred when a large flame propagates itself over the surface of the sample.

### 7.3 Determination of flash point of suspensions of solids and highly viscous materials

7.3.1 Bring the material to be tested and the tester to a temperature of 15° + 5° C (60° + 10° F) or 11° C (20° F) lower than the estimated flash point, whichever is lower. Turn the stirrer 250 + 10 rpm, stirring in a downward direction. Raise the temperature throughout the duration of the test at a rate of not less than 1° nor more than 1.5° F (2 to 3° F)/min. With the exception of these requirements for rates of stirring and heating, proceed as prescribed in Section 7.2.

### 7.4 Calculation and report

7.4.1 Observe and record the ambient barometric pressure at the time of the test. When the pressure differs from 760 mm Hg (101.3 kPa), correct the flash point as follows:

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$$(A) \text{ Corrected flash point} = C + 0.25 (101.3 - p)$$

$$(B) \text{ Corrected flash point} = F + 0.06 (760 - P)$$

$$(C) \text{ Corrected flash point} = C + 0.033 (760 - P)$$

where:

F = observed flash point, °F

C = observed flash point, °C

P = ambient barometric pressure, mm Hg

p = ambient barometric pressure, kPa.

NOTE: The barometric pressure used in this calculation must be the ambient pressure for the laboratory at the time of test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings. These must not be used.

7.4.2 Record the corrected flash point to the nearest 0.5° C (or 1° F).

7.4.3 Report the recorded flash point as the Pensky-Martens Closed Cup Flash Point ASTM D93 - IP 34, of the sample tested.

7.5 Refer to Method ASTM D93 77 for more details and background on the Pensky-Marten method.

#### 8.0 Quality Control

8.1 All quality control data should be available for review.

8.2 Duplicates and standard reference materials should be routinely analyzed.

8.3 The flash point of the p-xylene reference standard must be determined in duplicate at least once per sample batch. The average of the two analyses should be  $27^{\circ} \pm 0.8^{\circ} \text{ C}$  ( $81^{\circ} \pm 1.5^{\circ} \text{ F}$ ).

# METHOD 1020<sup>1</sup>

## SETAFLASH CLOSED-CUP METHOD

### 1.0 Scope and Application

1.1 Method 1020 make use of the Setaflash<sup>®</sup> Closed Tester to determine the flash point of paints, enamels, lacquers, varnishes, and related products and their components that have flash points between 0° and 110° C (32° and 230° F) and a viscosity lower than 150 stokes at 25° C (77° F). Tests at higher or lower temperatures are possible.

1.2 The procedures may be used to determine whether a material will or will not flash at a specified temperature or to determine the finite temperature at which a material will flash.

### 2.0 Summary of Method

2.1 By means of a syringe, 2 ml of sample is introduced through a leakproof entry port into the tightly closed Setaflash Tester or directly into the cup that has been brought to within 3° C (5° F) below the expected flash point.

2.2 As a flash/no flash test, the expected flash point temperature may be a specification (e.g., 60° C). For specification testing, the temperature of the apparatus is raised to the precise temperature of the expected flash point by slight adjustment of the temperature dial. After 1 min, a test flame is applied inside the cup and note is taken as to whether the test sample flashes or not. If a repeat test is necessary, a fresh sample should be used.

2.3 For a finite flash measurement, the temperature is sequentially increased through the anticipated range, the test flame being applied at 5° C (9° F) intervals until a flash is observed. A repeat determination is then made using a fresh sample, starting the test at the temperature of the last interval before the flash point of the material and making tests at increasing 0.5° C (1° F) intervals.

### 3.0 Interferences

3.1 Ambient pressure, sample homogeneity, drafts, and operator bias can affect flash point values.

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<sup>1</sup>This method is based on ASTM Method D327-78.

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### 4.0 Apparatus and Materials

4.1 Setaflash Tester as described in Appendix XI of ASTM Method 3278-78.

4.2 Thermometers conforming to specifications given in ASTM Method 3278-78. Test to determine that the scale error does not exceed 0.25° C (0.5° F). A magnifying lens significantly assists in making temperature observations.

4.3 Glass syringe: 2 ± 0.1-ml capacity at 25° C (77° F), to provide a means of taking a uniform sample. Check the capacity by discharging water into a weighing bottle and weighing. Adjust plunger if necessary. A disposable syringe of equal precision may be used.

4.4 Cooling block: Aluminum (described in Appendix X2 of ASTM D3278-78) which fits snugly within the test cup for rapid cooling of the sample cup.

4.5 Barometer.

### 5.0 Reagents

5.1 p-Xylene: Reference standard for checking the Setaflash Tester.

5.2 Cooling mixture of ice water or dry ice (solid CO<sub>2</sub>) and acetone.

5.3 Liquefied petroleum gas.

5.4 Heat transfer paste.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected employing a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 The sample size for each test is 2 ml. Obtain at least a 25-ml sample from the bulk source and store in a nearly full, tightly closed clean glass container or in another container suitable for the type of liquid being sampled.

6.3 Erroneously high flash points may be obtained if precautions are not taken to avoid loss of volatile materials. Do not open sample containers unnecessarily and do not transfer the sample to the cup unless its temperature is at least 10° C (20° F) below the expected flash point. Discard samples in leaky containers.

6.4 Do not use plastic bottles since certain volatile compounds can diffuse through the walls of the bottle.

## 7.0 Procedure

7.1 Prior to initial use and after removal of the thermometer, insert the thermometer into its pocket with a good heat transfer paste.

7.2 To help in making the necessary settings during a test, determine the relationship between the temperature control dial and thermometer readings at intervals not over 5° C (10° F) throughout the scale range of the heater before the initial use.

7.3 Place the tester in a subdued light and in a position where it is not exposed to disturbing drafts. Provide a black-coated shield, if necessary.

7.4 Read the manufacturer's operating and maintenance instructions on the care and servicing of the tester. Observe the specific suggestions regarding the operation of its various controls.

7.5 Check the accuracy of the tester by determining the flash point of the p-xylene reference standard in duplicate (Appendix X3). The average of the results should be 27.2° + 0.8° C (81° + 1.5° F). If not, remove the thermometer and observe whether sufficient heat transfer paste surrounds the thermometer to provide good heat transfer from the cup to the thermometer.

7.6 Ambient to 110° C (230° F).

7.6.1 Inspect the inside of the test cup, lid, and shutter mechanism for cleanliness and freedom from contamination. Use an absorbent tissue to wipe clean, if necessary. Lock the cover lid tightly in place.

7.6.2 Switch the tester on, if not already at stand-by. To rapidly approach the specification flash temperature of the charged sample, turn the heater dial fully clockwise causing the heater signal (red) light to glow. When the thermometer indicates a temperature of about 3° C (5° F) below the specification or target flash point temperature, reduce the heat input to the test cup by slowly turning the heater control dial counter-clockwise until the signal light goes out.  
NOTE: When the correct temperature is dialed on the temperature controller, the elapsed time to reach it may be greater than when turned full on, but less attention will be required in the intervening period.  
NOTE: The test cup temperature is stable when the signal light slowly cycles on and off.

7.6.3 Determine the barometric pressure to determine the corrected specification temperature at that barometric pressure.

7.6.4 After the test cup temperature has stabilized at the specification or target flash point, charge the syringe with the sample to be tested and transfer the syringe to the filling orifice, taking care not to lose any sample. Discharge the sample into the test cup by depressing

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the syringe plunger to its lowest position, then remove the syringe. If the sample has a viscosity greater than 45 SUS at 37.8° C (100° F) or equivalent of 9.5 cSt at 25° C (77° F), discharge the contents of the syringe directly into the cup. Immediately close tightly the lid and shutter assembly.

7.6.5 Set the 1-min timing device by rotating its knob clockwise to the required setting. In the meantime, open the gas control valve and light the pilot and the test flames. Adjust the test flame size with the pinch valve so as to match the size of the 5/32-in. (4-mm) diameter flame gauge.

7.6.6 After 1 min has elapsed, observe the temperature. If at the specification temperature (accounting for the differences of the barometer reading from 760 mm), apply the test flame by slowly and uniformly opening the slide fully and closing completely over a period of approximately 2-1/2 sec. Watch for a flash. (NOTE: The sample is considered to have flashed only if a comparatively large blue flame appears and propagates itself over the surface of the liquid. Occasionally, particularly near the actual flash point temperature, application of the test flame may give rise to a halo; this should be ignored.)

7.6.7 Turn off the test and the pilot flame. Clean the apparatus in preparation for the next test.

#### 7.7 0° C (32° F) to ambient

7.7.1 If the specification or target flash point is at or below ambient temperature, cool the sample to 5° to 10° C (10° to 20° F) below that point by some convenient means.

7.7.2 Cool the tester to the approximate temperature of the sample by inserting the cooling block filled with a cooling mixture into the sample well. Dry the cup with a paper tissue to remove any collected moisture prior to adding the sample. (CAUTION: Be careful in handling the cooling mixture and cooling block; wear gloves and goggles. Mixtures such as dry ice and acetone can produce severe frost bite.) (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.)

7.7.3 Introduce the sample as in 7.6.4. Allow the temperature to rise under ambient conditions or increase the temperature of the cup by rotating the heater controller clockwise slowly until the specification temperature adjusted for barometric pressure is reached. Determine whether the sample flashes as in 7.6.5 and 7.6.6.

7.7.4 Turn off the test and pilot flames. Clean up the apparatus.

## 7.8 Ambient to 110° C (230° F)

7.8.1 Preliminary or trial test: Follow steps 7.6.2 to 7.6.5 omitting the barometric reading and using an estimated finite flash point instead of a specification flash point temperature.

7.8.2 After 1 min has elapsed, observe the temperature, apply the test flame by slowly and uniformly opening the slide fully and closing completely over a period of 2-1/2 sec. Watch for a flash. (NOTE: The sample is considered to have flashed only if a comparatively large blue flame appears and propagates itself over the surface of the liquid. Occasionally, particularly near the actual flash point temperature, application of the test flame may give rise to a halo; this should be ignored.)

7.8.3 Finite flash point: If a flash is observed, proceed as below.

7.8.3.1 Using a temperature of 5° C (9° F) lower than the temperature observed in 7.8.2, repeat 7.8.1 and 7.8.2. (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.) If a flash is still observed, repeat at 5° C (9° F) lower intervals until no flash is observed. (NOTE: Never make a repeat test on the same sample. Always take a fresh portion for each test.)

7.8.3.2 Repeat 7.8.1 and 7.8.2 with a new sample, stabilizing the test cup temperature at the temperature at which no flash occurred previously. Observe whether a flash occurs at this temperature. If no flash occurs, increase the temperature at 0.5° C (1° F) intervals by making small incremental adjustment to the temperature controller and allowing 1-min intervals between each increment and the flash point test. Record the temperature at which the flash actually occurs. Record the barometric pressure. Turn off pilot and test flames and clean up tester.

7.8.4 Finite flash point: If no flash point is observed in 7.8.2, proceed as follows.

7.8.4.1 Using a test temperature of 5° C (9° F) higher than the temperature observed in 7.8.2, repeat steps 7.8.1 and 7.8.2. (NOTE: Never make a repeat test on the same sample. Always take a fresh portion for each test.) If no flash is observed, repeat at 5° C (9° F) higher intervals until a flash is observed.

7.8.4.2 Repeat step 7.8.3.2 with a new sample.

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### 7.9 0° C (32° F) to ambient temperature

7.9.1 Preliminary or trial test: Cool the sample to 3° to 5° C (5° to 10° F) below the expected flash point.

7.9.2 Cool the tester to approximately the temperature of the sample by inserting the cooling block filled with a cooling medium into the sample well.

7.9.3 Insert the sample as in 7.6.4. Set the 1-min timing device. After 1 min, apply the test flame by slowly and uniformly opening the side fully and closing completely over a period of approximately 2-1/2 sec. Observe for a flash. Record the temperature.

7.9.4 Finite flash point: If a flash is observed, proceed as follows.

7.9.4.1 Cool a new sample and the sample cup to 5° C (9° F) below the previous temperature (7.9.3). After 1 min, check for a flash as in 7.9.3. If the sample flashes, repeat test at 5° C (9° F) lower intervals until no flash is observed.

7.9.4.2 Repeat with a new sample, cooling both sample and tester to the temperature at which the sample did not flash. After 1 min, observe whether a flash occurs at this temperature. If not, increase the temperature at 0.5° C (1° F) intervals by making small incremental adjustments to the temperature controller, allowing 1 min between each increment and the test for the flash point. Record the temperature at which the flash actually occurs. Record the barometric pressure.

7.9.5 Finite flash point: If no flash point is observed proceed as follows.

7.9.5.1 Using a test temperature of 5° C (9° F) higher than the temperature observed in 7.9.3, repeat step 7.9.3. (CAUTION: Be careful in inserting the cooling block into the tester cup to prevent damage to the cup.) If no flash is observed, repeat at 5° C (9° F) higher intervals until flash is observed.

7.9.5.2 Using a new sample, repeat 7.9.4.2 until a flash occurs. Record the temperature at which the flash occurs and the barometric pressure.

### 7.10 Cleanup of apparatus and preparation for next test

7.10.1 To prepare for the next test, unlock the lid assembly of the tester and raise to the hinge stop. Soak up liquid samples with an

absorbent paper tissue and wipe dry. Clean the underside of the lid and filling orifice. A pipe cleaner may be of assistance in cleaning the orifice.

7.10.2 If the sample is a viscous liquid or contains dispersed solids, after soaking up most of the sample add a small amount of a suitable solvent for the sample to the cup and then soak up the solvent and wipe clean the interior surfaces of the cup with an absorbent tissue paper. (NOTE: If necessary to remove residual high boiling solvent residues, moisten tissue with acetone and wipe clean.) (NOTE: If any further cleaning is necessary, remove the lid and shutter assembly. Disconnect the silicone rubber hose and slide the lid assembly to the right to remove. If warm, handle carefully.)

7.10.3 After the cup has been cleaned, its temperature may be rapidly increased to some stand-by value by turning the temperature control dial to an appropriate point. (NOTE: It is convenient to hold the test cup at some stand-by temperature (depending on planned usage) to conserve time in bringing the cup within the test temperature range. The cup temperature may be quickly lowered by inserting the aluminum cooling block filled with an appropriate cooling mixture into the cup.)

7.10.4 The syringe is easily cleaned by filling it several times with acetone or any compatible solvent, discharging the solvent each time, and allowing the syringe to air dry with the plunger removed. Replace the plunger, and pump several times to replace any solvent vapor with air.

## 7.11 Correction for barometric pressure

7.11.1 When the barometric pressure differs from 760 mm Hg (101.3 kPa), calculate the flash point temperature by means of the following equations:

$$\begin{aligned}\text{Calculated flash point} &= C + 0.03 (760 - P) \\ &= F + 0.06 (760 - P)\end{aligned}$$

where:

C, F = observed flash point (°C or °F)  
P = barometric pressure (mm Hg).

7.11.2 Likewise determine the corrected specification flash point by the following equation:

$$\begin{aligned}C &= S - 0.03 (760 - P) \\ F &= S - 0.06 (760 - P)\end{aligned}$$

## 8 / CHARACTERISTICS - Ignitability; Corrosivity

where:

- C, F = flash point to be observed to obtain the specification flash point at standard pressure (S)
- S = specification flash point.

### 7.12 Report

7.12.1 When using the flash/no flash method, report whether the sample flashed at the required flash point and that the flash/no flash method was used.

7.12.2 If an actual flash point was determined, report the average of duplicate runs to nearest 0.5° C (1° F) provided the difference between the two values does not exceed 1° C (2° F).

## 8.0 Quality Control

8.1 All quality control data should be available for review.

8.2 Duplicates and standard reference materials should be routinely analyzed.

8.3 The flash point of the p-xylene reference standard must be determined in duplicate at least once per sample batch. The average of the two analyses should be  $27^{\circ} \pm 0.8^{\circ} \text{ C}$  ( $81^{\circ} \pm 1.5^{\circ} \text{ F}$ ).

## 2.1.2 Corrosivity

### Introduction

The corrosivity characteristic, as defined in 40 CFR 261.22, is designed to identify wastes which might pose a hazard to human health or the environment due to their ability to:

1. Mobilize toxic metals if discharged into a landfill environment,
2. Corrode handling, storage, transportation, and management equipment, or
3. Destroy human or animal tissue in the event of inadvertent contact.

In order to identify such potentially hazardous materials, EPA has selected two properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 1020 steel.

The following sections present the regulatory background and the regulation pertaining to the definition of corrosivity. The procedures for measuring pH of aqueous wastes are detailed in Methods 9040 and 9041. Method 1110 describes how to determine whether a waste is corrosive to steel.

### Regulatory Definition

The following material has been taken nearly verbatim from the RCRA regulations.

1. A solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has either of the following properties:
  - a. It is aqueous and has a pH less than or equal to 2 or greater than or equal to 12.5, as determined by a pH meter using either the test method specified in this manual (Method 9040) (also described in "Methods for Analysis of Water and Wastes" EPA 600/4-79-020, March 1979), or an equivalent test method approved by the Administrator under the procedures set forth in §§260.20 and 260.21.
  - b. It is a liquid and corrodes steel (SAE 1020) at a rate greater than 6.35 mm (0.250 inch) per year at a test temperature of 55° C (130° F) as determined by the test method specified in NACE (National Association of Corrosion Engineers) Standard TM-01-69 as standardized in this manual (Method 1110) or an

## 2 / CHARACTERISTICS - Corrosivity

equivalent test method approved by the Administrator under the procedures set forth in §§260.20 and 260.21.

2. A solid waste that exhibits the characteristic of corrosivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D002.

## METHOD 1110

### CORROSIVITY TOWARD STEEL

#### 1.0 Introduction

1.1 Method 1110<sup>1</sup> is used to measure the corrosivity toward steel of both aqueous and nonaqueous liquid wastes.

#### 2.0 Summary of Method

2.1 This test exposes coupons of SAE Type 1020 steel to the liquid waste to be evaluated and, by measuring the degree to which the coupon has been dissolved, determines the corrosivity of the waste.

#### 3.0 Interferences

3.1 In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within  $\pm 10\%$ . However, large differences in corrosion rates may occasionally occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.

#### 4.0 Apparatus and Materials

4.1 A versatile and convenient apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5000 milliliters), a reflux condenser, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type test is shown in Figure 1.

4.2 The supporting device and container should not be affected by or cause contamination of the waste under test.

4.3 The method of supporting the coupons will vary with the apparatus used for conducting the test but should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include glass, fluorocarbon or coated metal.

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<sup>1</sup>This method is based on NACE Standard TM-01-69 (1972 Revision), "Laboratory Corrosion Testing of Metals for the Process Industries," National Association of Corrosion Engineers, 3400 West Loop South, Houston, TX 77027.

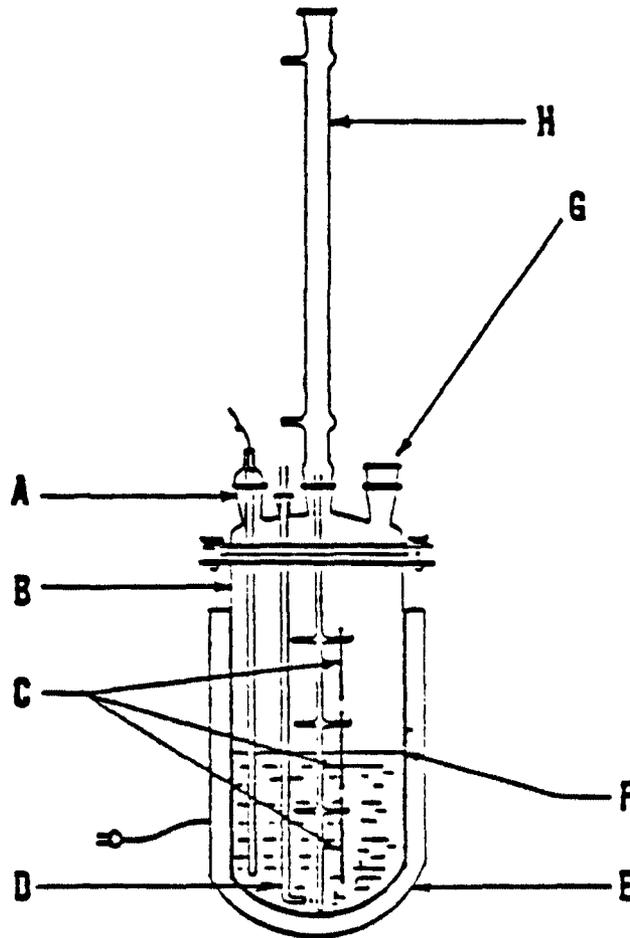


Figure 1. Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens hung on supporting device, D = gas inlet, E = heating mantle, F = liquid interface, G = opening in flask for additional apparatus that may be required, and H = reflux condenser.

4.4 The shape and form of the coupon support should ensure free contact with the waste.

4.5 A circular specimen of SAE 1020 steel of about 3.75 cm (1.5 inch) diameter is a convenient shape for a coupon. With a thickness of approximately 0.32 cm (0.125 inch) and a 0.80-cm (0.4-in.) diameter hole for mounting, these specimens will readily pass through a 45/50 ground glass joint of a distillation kettle. The total surface area of a circular specimen is given by the following equation:

$$A = 3.14/2(D^2 - d^2) + (t)(3.14)(D) + (t)(3.14)(d)$$

where t = thickness, D = diameter of the specimen, and d = diameter of the mounting hole. If the hole is completely covered by the mounting support, the last term  $(t)(3.14)(d)$  in the equation is omitted.

4.5.1 All coupons should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to  $\pm 1\%$  is usually adequate.

4.5.2 More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the waste. This can be accomplished either by chemical treatment (pickling), electrolytic removal, or by grinding with a coarse abrasive. At least 0.254 mm (0.0001 inch) or 2 to 3 mg/cm<sup>2</sup> should be removed. Final surface treatment should include finishing with #120 abrasive paper or cloth. Final cleaning consists of scrubbing with bleachfree scouring powder, followed by rinsing in distilled water, then acetone or methanol, and finally air drying. After final cleaning, the coupon should be stored in a desiccator until used.

4.5.3 The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 ml/cm<sup>2</sup>.

## 5.0 Reagents

- 5.1 Sodium hydroxide (20%).
- 5.2 Zinc dust.
- 5.3 Concentrated hydrochloric acid.
- 5.4 Stannous chloride.
- 5.5 Antimony chloride.

## 6.0 Sample Collection, Presentation, and Handling

6.1 All samples should be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

## 7.0 Procedure

7.1 Assemble the test apparatus as described in Section 4.0 above.

7.2 Fill the container with the appropriate amount of waste.

7.3 Begin agitation at a rate sufficient to ensure that the liquid is kept well mixed and homogeneous.

7.4 Using the heating device bring the temperature of the waste to 55° C (130° F).

7.5 An accurate rate of corrosion is not required but only a determination as to whether the rate of corrosion is less than or greater than 6.35 mm per year. A 24-hour test period should be ample to determine whether or not the rate of corrosion is greater than 6.35 mm per year.

7.6 In order to accurately determine the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical and electrolytic.

7.6.1 Mechanical cleaning includes scrubbing, scraping, brushing and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods. The others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

7.6.2 Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease or resinous materials, and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

<u>Solution</u>	<u>Soaking Time</u>	<u>Temperature</u>
20% NaOH + 200 g/l zinc dust	5 min	Boiling
or		
Conc. HCl + 50 g/l SnCl <sub>2</sub> + 20 g/l SbCl <sub>3</sub>	Until clean	Cold

7.6.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed is:

Solution	50 g/l H <sub>2</sub> SO <sub>4</sub>
Anode	Carbon or lead
Cathode	Steel coupon
Cathode current density	20 amp/cm <sup>2</sup> (129 amp/in. <sup>2</sup> )
Inhibitor	2 cc organic inhibitor/liter
Temperature	74° C (165° F)
Exposure Period	3 minutes

NOTE: Precautions must be taken to ensure good electrical contact with the coupon, to avoid contamination of the cleaning solution with easily reducible metal ions, and to ensure that inhibitor decomposition has not occurred. Instead of using a proprietary inhibitor, 0.5 g/l or either diorthotolyl thiourea or quinolin ethiodide can be used.

7.7 Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7.8 After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a measure of corrosion requires making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for the purpose of this regulation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{weight loss} \times 11.145}{\text{area} \times \text{time}}$$

where weight loss is in milligrams, area in square centimeters, time in hours, and corrosion rate in millimeters per year (mmpy).

## 8.0 Quality Control

8.1 All quality control data should be filed and available for auditing.

8.2 Duplicate samples should be analyzed on a routine basis.

## CHARACTERISTICS - Corrosivity; Reactivity

### 2.1.3 Reactivity

#### Introduction

The regulation in 40 CFR 261.23 defines reactive wastes to include wastes which have any of the following properties: (1) readily undergo violent chemical change; (2) react violently or form potentially explosive mixtures with water; (3) generate toxic fumes when mixed with water or, in the case of cyanide or sulfide-bearing wastes, when exposed to mild acidic or basic conditions; (4) explode when subjected to a strong initiating force; (5) explode at normal temperatures and pressures; or (6) fit within the Department of Transportation's forbidden explosives, Class A explosives, or Class B explosives classifications.

This definition is intended to identify wastes which, because of their extreme instability and tendency to react violently or explode, pose a problem at all stages of the waste management process. The definition is to a large extent a paraphrase of the narrative definition employed by the National Fire Protection Association. The Agency chose to rely on a descriptive, prose definition of reactivity because the available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies.

#### Regulatory Definition

##### Characteristic of Reactivity Regulation

A solid waste exhibits the characteristic of reactivity if a representative sample of the waste has any of the following properties:

1. It is normally unstable and readily undergoes violent change without detonating.
2. It reacts violently with water.
3. It forms potentially explosive mixtures with water.
4. When mixed with water, it generates toxic gases, vapors or fumes in a quantity sufficient to present a danger to human health or the environment.
5. It is a cyanide- or sulfide-bearing waste which, when exposed to pH conditions between 2 and 12.5, can generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment. (Methods 9010 and 9030 can be used to detect the presence of cyanide and sulfide in wastes.)
6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

## 2 / CHARACTERISTICS - Reactivity

7. It is readily capable of detonation or explosive decomposition or reaction at standard temperature and pressure.
8. It is a forbidden explosive as defined in 49 CFR 173.51, or a Class A explosive as defined in 49 CFR 173.53, or a Class B explosive as defined in 49 CFR 173.88.
9. A solid waste that exhibits the characteristic of reactivity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number of D003.

### Definition of Explosive Materials

For purposes of this regulation, a waste is a reactive waste by reason of explosivity if it meets one or more of the following descriptions:

1. Is explosive and ignites spontaneously or undergoes marked decomposition when subjected for 48 consecutive hours to a temperature of 75° C (167° F).
2. Firecrackers, flash crackers, salutes, or similar commercial devices which produce or are intended to produce an audible effect, the explosive content of which exceeds 12 grains each in weight; pest control bombs, the explosive content of which exceeds 18 grains each in weight; and any such devices, without respect to explosive content, which on functioning are liable to project or disperse metal, glass or brittle plastic fragments.
3. Fireworks that combine an explosive and a detonator or blasting cap.
4. Fireworks containing an ammonium salt and a chlorate.
5. Fireworks containing yellow or white phosphorus.
6. Fireworks or firework compositions that ignite spontaneously or undergo marked decomposition when subjected for 48 consecutive hours to a temperature of 75° C (167° F).
7. Toy torpedoes, the maximum outside dimension of which exceeds 7/8 inch, or toy torpedoes containing a mixture of potassium chlorate, black antimony and sulfur with an average weight of explosive composition in each torpedo exceeding four grains.
8. Toy torpedoes containing a cap composed of a mixture of red phosphorus and potassium chlorate exceeding an average of one-half (0.5) grain per cap.
9. Fireworks containing copper sulfate and a chlorate.

10. Explosives containing an ammonium salt and a chlorate.
11. Liquid nitroglycerin, diethylene glycol dinitrate or other liquid explosives not authorized.
12. Explosives condemned by the Bureau of Explosives (except properly packed samples for laboratory examinations).
13. Leaking or damaged packages of explosives.
14. Solid materials which can be caused to deflagrate by contact with sparks or flame such as produced by safety fuse or an electric squib, but cannot be detonated (see Note 1) by means of a No. 8 test blasting cap (see Note 2). Example: Black powder and low explosives.
15. Solid materials which contain a liquid ingredient, and which, when unconfined (see Note 3), can be detonated by means of a No. 8 test blasting cap (see Note 2); or which can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 inches or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 inches. Example: High explosives, commercial dynamite containing a liquid explosive ingredient.
16. Solid materials which contain no liquid ingredient and which can be detonated, when unconfined (see Note 3), by means of No. 8 test blasting cap (see Note 2); or which can be exploded in at least 50 percent of the trials in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of 4 inches or more, but cannot be exploded in more than 50 percent of the trials under a drop of less than 4 inches. Example: high explosives, commercial dynamite containing no liquid explosive ingredient, trinitrotoluene, amatol, tetryl, picric acid, ureanitate, pentolite, commercial boosters.
17. Solid materials which can be caused to detonate when unconfined (see Note 3), by contact with sparks or flame such as produced by safety fuse or an electric squib; or which can be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4), in more than 50 percent of the trials under a drop of less than 4 inches. Example: initiating and priming explosives, lead azide, fulminate of mercury, high explosives.
18. Liquids which may be detonated separately or when absorbed in sterile absorbent cotton, by a No. 8 test blasting cap (see Note 2); but which cannot be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4), by a drop of less than 10 inches. The liquid must not be significantly more volatile than nitroglycerine and must not freeze at temperatures above minus 10° F. Example: high explosives, desensitized nitroglycerine.

#### 4 / CHARACTERISTICS - Reactivity

19. Liquids that can be exploded in the Bureau of Explosives' Impact Apparatus (see Note 4) under a drop of less than 10 inches.  
Example: nitroglycerine.
20. Blasting caps. these are small tubes, usually made of an alloy of either copper or aluminum, or of molded plastic closed at one end and loaded with a charge of initiating or priming explosives. Blasting caps (see Note 5) which have been provided with a means for firing by an electric current, and sealed, are known as electric blasting caps.
21. Detonating primers which contain a detonator and an additional charge of explosives, all assembled in a suitable envelope.
22. Detonating fuses, which are used in the military service to detonate the high explosive bursting charges of projectiles, mines, bombs, torpedoes, and grenades. In addition to a powerful detonator, they may contain several ounces of a high explosive, such as tetryl or dry nitrocellulose, all assembled in a heavy steel envelope. They may also contain a small amount of radioactive component. Those that will not cause functioning of other fuses, explosives, or explosive devices in the same or adjacent containers are classes as class C explosives and are not reactive waste.
23. A shaped charge, consisting of a plastic, paper, or other suitable container comprising a charge of not to exceed 8 ounces of a high explosive containing no liquid explosive ingredient and with a hollowed-out portion (cavity) lined with a rigid material.
24. Ammunition or explosive projectiles, either fixed, semi-fixed or separate components which are made for use in cannon, mortar, howitzer, recoilless rifle, rocket, or other launching device with a caliber of 20 mm or larger.
25. Grenades. Grenades, hand or rifle, are small metal or other containers designed to be thrown by hand or projected from a rifle. They are filled with an explosive or a liquid, gas, or solid material such as a tear gas or an incendiary or smoke producing material and a bursting charge.
26. Explosive bombs. Explosive bombs are metal or other containers filled with explosives. They are used in warfare and include airplane bombs and depth bombs.
27. Explosive mines. Explosive mines are metal or composition containers filled with a high explosive.
28. Explosive torpedoes. Explosive torpedoes, such as those used in warfare, are metal devices containing a means of propulsion and a quantity of high explosives.

29. Rocket ammunition. Rocket ammunition (including guided missiles) is ammunition designed for launching from a tube, launcher, rails, trough, or other launching device, in which the propellant material is a solid propellant explosive. It consists of an igniter, rocket motor, and projectile (warhead) either fused or unfused, containing high explosives or chemicals.
30. Chemical ammunition. Chemical ammunition used in warfare is all kinds of explosive chemical projectiles, shells, bombs, grenades, etc., loaded with tear, or other gas, smoke or incendiary agent, also such miscellaneous apparatus as cloud-gas cylinders, smoke generators, etc., that may be utilized to project chemicals.
31. Boosters, bursters, and supplementary charges. Boosters and supplementary charges consist of a casing containing a high explosive and are used to increase the intensity of explosion of the detonator of a detonating fuse. Bursters consist of a casing containing a high explosive and are used to rupture a projectile or bomb to permit release of its contents.
32. Jet thrust units or other rocket motors containing a mixture of chemicals capable of burning rapidly and producing considerable pressure.
33. Propellant mixtures (i.e., any chemical mixtures which are designed to function by rapid combustion with little or no smoke).

NOTE 1: The detonation test is performed by placing the sample in an open-end fiber tube which is set on the end of a lead block approximately 1-1/2 in. in diameter and 4 in. high which, in turn, is placed on a solid base. A steel plate may be placed between the fiber tube and the lead block.

NOTE 2: A No. 8 test blasting cap is one containing two grams of a mixture of 80% mercury fulminate and 20% potassium chlorate, or a cap of equivalent strength.

NOTE 3: "Unconfined" as used in this section does not exclude the use of a paper or soft fiber tube wrapping to facilitate tests.

NOTE 4: The Bureau of Explosives' Impact Apparatus is a testing device designed so that a guided 8-lb weight may be dropped from predetermined heights so as to impact specific quantities of liquid or solid materials under fixed conditions. Detailed prints of the apparatus may be obtained from the Bureau of Explosives, Association of American Railroads, Operations and Maintenance Dept., Bureau of Explosives, American Railroad Building, Washington, D.C. 20036; 202-293-4048. The procedures for operating this apparatus are described in the following paragraphs.

Method for Testing Liquids. The anvil is inserted in the receptacle in the anvil housing. A new cup is dropped into the cup-positioning block. One drop of the sample liquid (about 0.01 g) is dropped into the cup

## 6 / CHARACTERISTICS - Reactivity; EP Toxicity

from a pipette and the cup is revolved until an even film forms on base. The top striker and the main striker are inserted as far as possible into the upper housing. The upper housing is then placed over the cup-positioning block so that the end of the main striker goes into the brass cup. When the upper housing is removed from the cup-positioning block, the brass cup is picked up on the end of the main striker. When the two housings are screwed together, the brass cup automatically rests firmly on the anvil.

An 8-lb drop weight is dropped from predetermined heights until consistent failure results using the new sample portion and cup each time. An explosion is evidenced by flame or flame and noise, but in either event the brass cup will be belled out or bulged.

After making the drop, the drop weight is raised, the test assembly removed, and appropriate solvent is poured into the top end. The two housings are then separated, the striker removed, and the brass cup removed from the striker end.

All solvent is removed carefully and thoroughly before preparations are started for next drop and the apparatus cooled and cleaned. The test is then repeated in the same manner, but with a filter paper disc in the base of the cup under the composition being tested.

Method for Testing Solids. The die is placed in the anvil assembly and a small amount (about 0.01 g)<sup>1</sup> to make a thin film is placed into the die assembly. The steel striker pellet (plug) is inserted carefully and then the striker (plunger). The assembly is then placed in the apparatus and the drop weight allowed to rest on the striker top to effect even distribution of the explosive.

The 8-lb drop weight is then dropped on the striker from predetermined heights until consistent failure results (i.e., explosion, etc.) using a new sample portion each time.

The die assembly is removed carefully and the striker removed. A few drops of appropriate solvent are poured into the die assembly before it is disassembled.

All parts are cleaned and dried carefully before each test.

NOTE 5: Blasting caps, blasting caps with safety fuse, or electric blasting caps in quantities of 1,000 or less are classified as class 0 explosives and not subject to regulation as a reactive waste.

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<sup>1</sup>It is suggested that a tiny spoon be devised to measure the proper amount of test sample, since this is much more convenient and safer than other methods of measuring the sample.

## 2.1.4 Extraction Procedure Toxicity

### Introduction

The Extraction Procedure (EP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. It is a laboratory test in which a representative sample of a waste is extracted with distilled water maintained at a pH of 5 using acetic acid. The extract obtained from the EP (the "EP Extract") is then analyzed to determine if any of the thresholds established for the eight elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver), four pesticides (Endrin, Lindane, Methoxychlor, Toxaphene), and two herbicides (2,4,5-trichlorophenoxypropionic acid, 2,4-dichlorophenoxyacetic acid) have been exceeded. If the EP Extract contains any one of the above substances in an amount equal to or exceeding the levels specified in 40 CFR 261.24, the waste possesses the characteristic of Extraction Procedure Toxicity and is a hazardous waste.

### Summary of Procedure

The Extraction Procedure consists of five steps (refer to Figure 1):

#### 1. Separation Procedure

A waste containing unbound liquid is filtered and if the solid phase is less than 0.5% of the waste, the solid phase is discarded and the filtrate analyzed for trace elements, pesticides, and herbicides (step 5). If the waste contains more than 0.5% solids, the solid phase is extracted and the liquid phase stored for later use.

#### 2. Structural Integrity Procedure/Particle Size Reduction

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of waste of 3.1 cm<sup>2</sup>, or, if it consists of a single piece, be subjected to the Structural Integrity Procedure. The Structural Integrity Procedure is used to demonstrate the ability of the waste to remain intact after disposal. If the waste does not meet one of these conditions it must be ground to pass the 9.5-mm sieve.

#### 3. Extraction of Solid Material

The solid material from step 2 is extracted for 24 hr in an aqueous medium whose pH is maintained at or below 5 using 0.5 N acetic acid. The pH is maintained either automatically or manually. (In acidifying to pH 5, no more than 4.0 g of acid solution per g of material being extracted may be used.)

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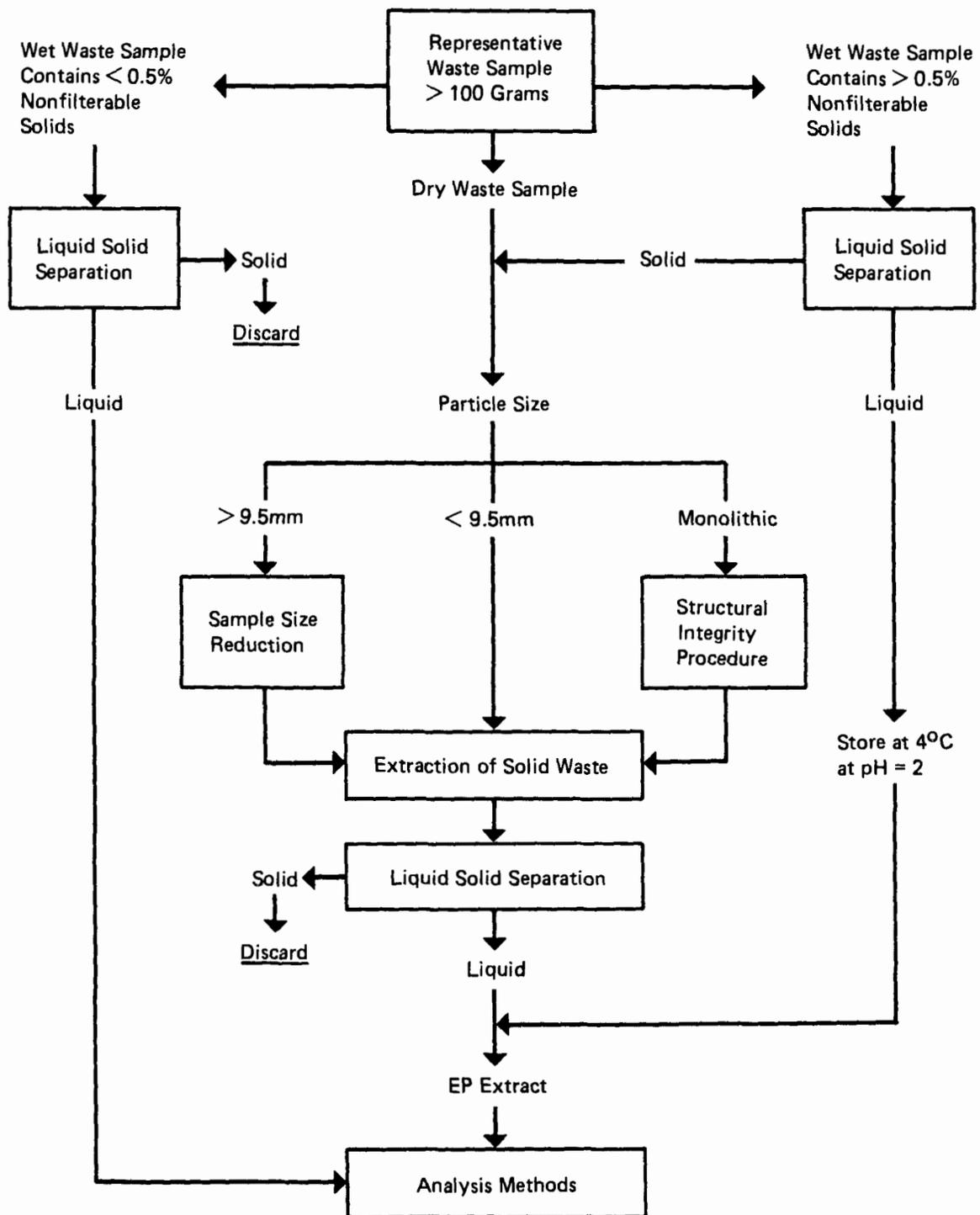


Figure 1. Extraction Procedure Flowchart.

4. Final Separation of the Extraction from the Remaining Solid

After extraction, the liquid:solid ratio is adjusted to 20:1 and the mixed solid and extraction liquid are separated by filtration. the solid is discarded and the liquid combined with any filtrate obtained in step 1. This is the EP Extract that is analyzed and compared to the threshold listed in Table 1 of 40 CFR 261.24.

5. Testing (Analysis) of EP Extract

Inorganic and organic species are identified and quantified using the appropriate methods in the 7000 and 8000 series of methods in this manual.

Regulatory Definition

A solid waste exhibits the characteristic of EP toxicity if, using the appropriate test methods described in this manual or equivalent methods approved by the Administrator under the procedures set forth in 40 CFR 260.20 and 260.21, the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at a concentration equal to or greater than the respective value given in that Table. If a waste contains less than 0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

A solid waste that exhibits the characteristic of EP toxicity, but is not listed as a hazardous waste in Subpart D, is assigned EPA Hazardous Waste Numbers that correspond to the toxic contaminants causing it to be hazardous. These numbers are specified in Table 1.

## 4 / CHARACTERISTICS - EP Toxicity

TABLE 1. MAXIMUM CONCENTRATION OF CONTAMINANTS  
FOR CHARACTERISTIC OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum concentration (mg/l)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10,10-Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethanonaph- thalene)	0.02
D013	Lindane (1,2,3,4,5,6- Hexachlorocyclohexane, gamma isomer)	0.4
D014	Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl)ethane)	10.0
D015	Toxaphene (C <sub>10</sub> H <sub>10</sub> Cl <sub>8</sub> , Technical chlorinated camphene, 67-69% chlorine)	0.5
D016	2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0
D017	2,4,5-TP (Silvex) (2,4,5- Trichlorophenoxypropionic acid)	1.0

## METHOD 1310

### EXTRACTION PROCEDURE (EP) TOXICITY TEST METHOD AND STRUCTURAL INTEGRITY TEST

#### 1.0 Scope and Application

1.1 The extraction procedure (EP) described in this method is designed to simulate the leaching a waste will undergo if disposed of in an improperly designed sanitary landfill. Method 1310 is applicable to liquid, solid, and multiphase samples.

#### 2.0 Summary of Method

2.1 If a representative sample of the waste contains more than 0.5% solids, the solid phase of the sample is extracted with deionized water which is maintained at a pH of  $5 \pm 0.2$  using acetic acid. The extract is analyzed to determine if any of the threshold limits listed in Table 1 are exceeded. Table 1 also specifies the approved method of analysis. Wastes that contain less than 0.5% solids are not subjected to extraction, but are directly analyzed and evaluated in a manner identical to that of extracts.

#### 3.0 Interferences

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods referenced in Table 1.

#### 4.0 Apparatus and Materials

4.1 Extractor: For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Examples of suitable extractors are shown in Figures 1-3 of this method and Section 2.2 (Mobility) of this manual and are available from Associated Designs & Manufacturing Co., Alexandria, Virginia; Glas-Col Apparatus Co., Terre Haute, Indiana; Millipore, Bedford, Massachusetts; and Rexnord, Milwaukee, Wisconsin.

4.2 pH Meter or pH Controller (Chemtrix, Inc., Hillsboro, Oregon is a possible source of a pH controller).

4.3 Filter holder: A filter holder capable of supporting a 0.45- $\mu$  filter membrane and able to withstand the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex systems that can exert up to 5.3 kg/cm<sup>3</sup> (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to EPA and deemed suitable for use are listed in Table 2.

TABLE 1. MAXIMUM CONCENTRATION OF CONTAMINANTS  
FOR CHARACTERISTIC OF EP TOXICITY

Contaminant	Maximum concentration (mg/l)	Analytical method
Arsenic	5.0	7060, 7061
Barium	100.0	7080, 7081
Cadmium	1.0	7130, 7131
Total Chromium	5.0	7190, 7191
Hexavalent Chromium	5.0	7195, 7196, 7197
Lead	5.0	7420, 7421
Mercury	0.2	7470
Selenium	1.0	7740, 7741
Silver	5.0	7760, 7761
Endrin (1,2,3,4,10,10-Hexachloro-1 7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1 4-endo, endo-5,8-dimethanonaph- thalene)	0.02	8080
Lindane (1,2,3,4,5,6- Hexachlorocyclohexane, gamma isomer)	0.4	8080
Methoxychlor (1,1,1-Trichloro-2,2-bis (p-methoxyphenyl)ethane)	10.0	8080
Toxaphene (C <sub>10</sub> H <sub>10</sub> Cl <sub>8</sub> , Technical chlorinated camphene, 67-69% chlorine)	0.5	8080
2,4-D (2,4-Dichlorophenoxyacetic acid)	10.0	8150
2,4,5-TP (Silvex) (2,4,5- Trichlorophenoxypropionic acid)	1.0	8150

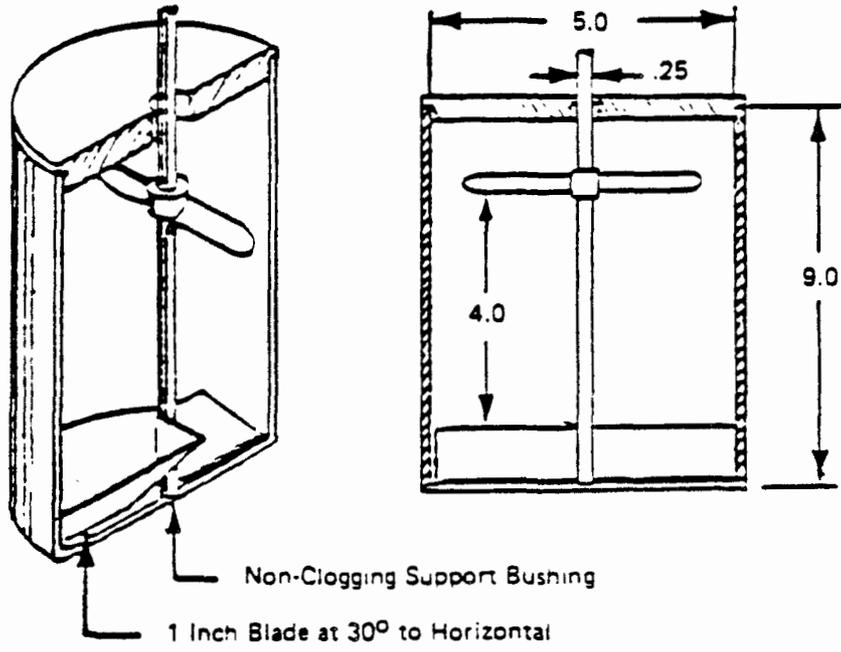


Figure 1. Extractor.

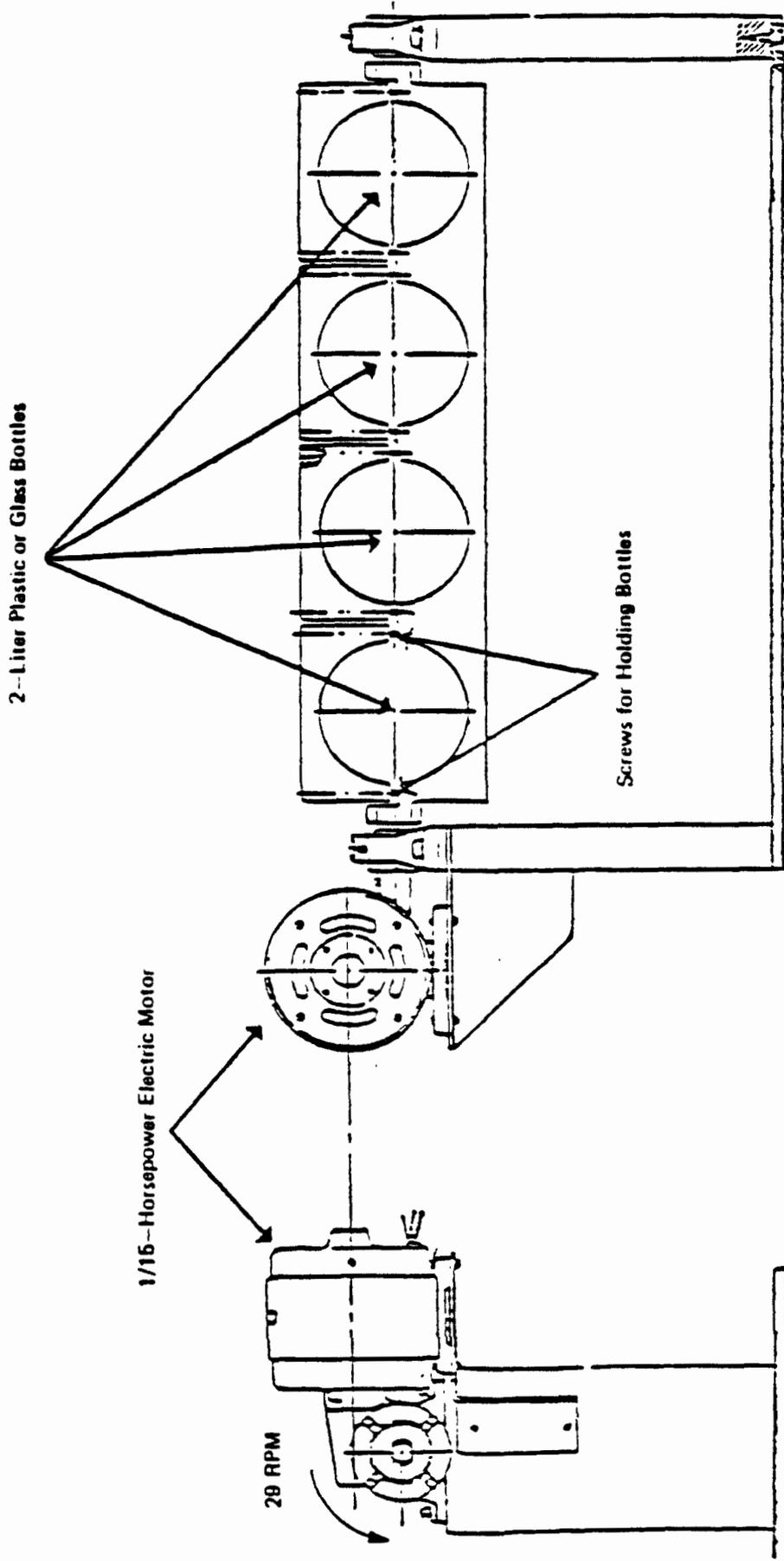


Figure 2. Rotary Extractor.

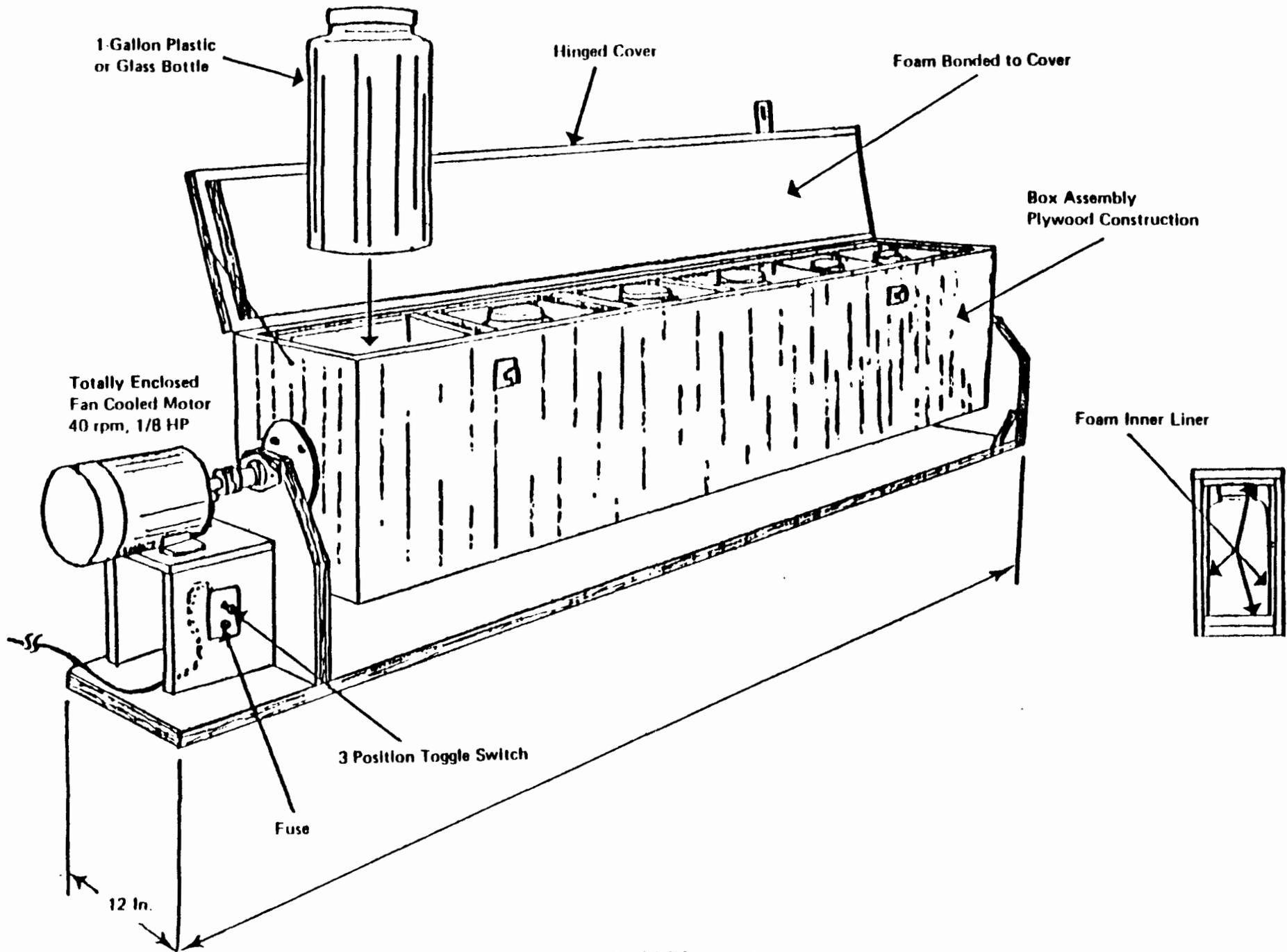


Figure 3. FPRI extractor.

4.4 Filter membrane: Filter membrane suitable for conducting the required filtration shall be fabricated from a material which: (1) is not physically changed by the waste material to be filtered, and (2) does not absorb or leach the chemical species for which a waste's EP Extract will be analyzed. Table 3 lists filter media known to the agency and generally found to be suitable for solid waste testing.

4.4.1 In cases of doubt, contact the filter manufacturer to determine if the membrane or the prefilter are adversely affected by the particular waste. If no information is available, submerge the filter in the waste's liquid phase. After 48 hr, a filter that undergoes visible physical change (i.e., curls, dissolves, shrinks, or swells) is unsuitable for use.

TABLE 2. EPA-APPROVED FILTER HOLDERS

Manufacturer	Size	Model No.	Comments
<u>Vacuum Filters</u>			
Nalgene	500 ml	44-0045	Disposable plastic unit, includes prefilter and filter pads, and reservoir; should be used when solution is to be analyzed for inorganic constituents
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
<u>Pressure Filters</u>			
Nuclepore	142 mm	425900	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

TABLE 3. EPA-APPROVED FILTRATION MEDIA

Supplier	Filter to be used for aqueous systems	Filter to be used for organic systems
<u>Coarse Prefilter</u>		
Gelman	61631, 61635	61631, 61635
Nuclepore	210907, 211707	210907, 211707
Millipore	AP25 035 00, AP25 127 50	AP25 035 00, AP25 127 50
<u>Medium prefilters</u>		
Nuclepore	210905, 211705	210905, 211705
Millipore	AP20 035 00, AP20 124 50	AP20 035 00, AP20 124 50
<u>Fine prefilters</u>		
Gelman	64798, 64803	64798, 64803
Nuclepore	210903, 211703	210903, 211703
Millipore	AP15 035 00, AP15 124 50	AP15 035 00, AP15 124 50
<u>Fine filters (0.45 <math>\mu</math>m)</u>		
Gelman	60173, 60177	60540 or 66149, 60544 or 66151
Pall	NX04750, NX14225	
Nuclepore	142218	142218 <sup>a</sup>
Millipore	HAWP 047 00, HAWP 142 50	FHUP 047 00, FHLP 142 50
Selas	83485-02, 83486-02	83485-02, 83486-02

<sup>a</sup>Susceptible to decomposition by certain polar organic solvents.

4.4.2.1 Prepare a standard solution of the chemical species of interest.

4.4.2.2 Analyze the standard for its concentration of the chemical species.

4.4.2.3 Filter the standard and re-analyze. If the concentration of the filtrate differs from the original standard, the filter membrane leaches or absorbs one or more of the chemical species.

4.5 Structural integrity tester: Having a 3.18-cm (1.25-in.) diameter hammer weighing 0.33 kg (0.73 lb) and having a free fall of 15.24 cm (6 in.) shall be used. This device is available from Associated Design and Manufacturing Company, Alexandria, VA 22314, as Part No. 125, or it may be fabricated to meet the specifications shown in Figure 4.

## 5.0 Reagents

5.1 Deionized water: Water should be monitored for impurities.

5.2 0.5 N acetic acid: This can be made by diluting concentrated glacial acetic acid (17.5 N). The glacial acetic acid should be of high purity and monitored for impurities.

5.3 Analytical standards should be prepared according to the analytical methods referenced in Table 1.

## 6.0 Sample Collection, Preservation and Handling

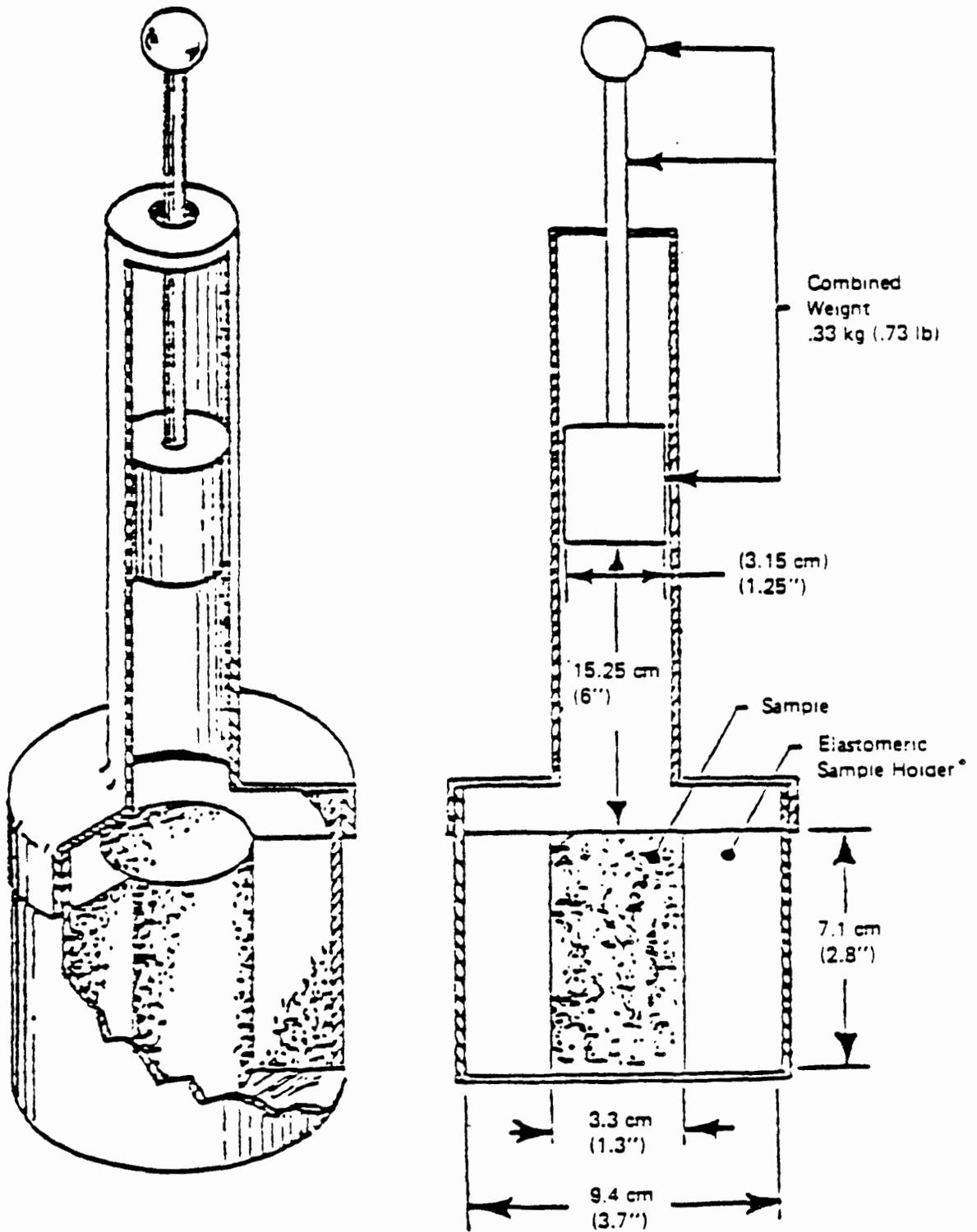
6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Preservatives must not be added to samples.

6.3 Samples can be refrigerated if it is determined that refrigeration will not affect the integrity of the sample.

## 7.0 Procedure

7.1 If the waste does not contain any free liquid, go to Section 7.9. If the sample is liquid or multiphase, continue as follows. Weigh filter membrane and prefilter to +0.01 g. Handle membrane and prefilters with blunt curved-tip forceps or vacuum tweezers, or by applying suction with a pipette.



\* Elastomeric sample holder fabricated of material firm enough to support the sample.

Figure 4. Compaction tester.

7.2 Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45- $\mu$ m membrane on the support screen and add prefilters in ascending order of pore size. Do not prewet filter membrane.

7.3 Weigh out a representative subsample of the waste (100 g minimum).

7.4 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration.

7.5 Wet the filter with a small portion of the waste's or extraction mixture's liquid phase. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10-psi increments to 75 psi. Halt filtration when liquid flow stops. This liquid will constitute part or all of the extract (refer to Section 7.16). The liquid should be refrigerated until time of analysis.

NOTE: Oil samples or samples which contain oil are treated in exactly the same way as any other sample. The liquid portion of the sample is filtered and treated as part of the EP extract. If the liquid portion of the sample will not filter (this is usually the case with heavy oils or greases) it is carried through the EP extraction as a solid.

7.6 Remove the solid phase and filter media and, while not allowing it to dry, weight to +0.01 g. The wet weight of the residue is determined by calculating the weight difference between the weight of the filters (Section 7.1) and the weight of the solid phase and the filter media.

7.7 The waste will be handled differently from this point on depending on whether it contains more or less than 0.5% solids. If the sample appears to have less than 0.5% solids, the percent solids will be determined by the following procedure.

7.7.1 Dry the filter and residue at 80° C until two successive weighings yield the same value.

7.7.2 Calculate the percent solids using the following equation:

$$\frac{\text{weight of filtered solid and filters} - \text{tared weight of filters}}{\text{initial weight of waste material}} \times 100 = \% \text{ solids}$$

NOTE: This procedure is only used to determine whether the solid must be extracted or whether it can be discarded unextracted. It

is not used in calculating the amount of water or acid to use in the extraction step. Do not extract solid material that has been dried at 80° C. A new sample will have to be used for extraction if a percent solids determination is performed.

7.8 If the solid comprises less than 0.5% of the waste, discard the solid and proceed immediately to Section 7.17, treating the liquid phase as the extract.

7.9 The solid material obtained from Section 7.5 and all materials that do not contain free liquids should be evaluated for particle size. If the solid material has a surface area per gram of material equal to or greater than 3.1 cm<sup>2</sup> or passes through a 9.5-mm (0.375-in.) standard sieve, the operator should proceed to Section 7.11. If the surface area is smaller or the particle size larger than specified above, the solid material would be prepared for extraction by crushing, cutting or grinding the material so that it passes through a 9.5-mm (0.375-in.) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described in Section 7.10.

#### 7.10 Structural Integrity Procedure (SIP):

7.10.1 Cut a 3.3-cm-diameter by 7.1-cm-long cylinder from the waste material. For wastes that have been treated using a fixation process, the waste may be cast in the form of a cylinder and allowed to cure for 30 days prior to testing.

7.10.2 Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 additional times.

7.10.3 Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 g and transfer it to the Extractor.

7.11 If the sample contains more than 0.5% solids, use the wet weight of the solid phase obtained in Section 7.6 for purposes of calculating the amount of liquid and acid to employ for extraction by using the following equation:

$$W = W_f - W_t$$

where:

W = wet weight in grams of solid to be charged to extractor

W<sub>f</sub> = wet weight in grams of filtered solids and filter media

W<sub>t</sub> = weight in grams of tared filters.

If the waste does not contain any free liquids, 100 g of the material will be subjected to the extraction procedure.

7.12 Place the appropriate amount of material (refer to Section 7.11) into the extractor and add 16 times its weight of deionized water.

7.13 After the solid material and deionized water are placed in the extractor, the operator should begin agitation and measure the pH of the solution in the extractor. If the pH is greater than 5.0, the pH of the solution should be decreased to  $5.0 \pm 0.2$  by adding 0.5 N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and, if the pH rises above 5.2, 0.5 N acetic acid should be added to bring the pH down to  $5.0 \pm 0.2$ . However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture should be agitated for 24 hr and maintained at  $20^{\circ}$ - $40^{\circ}$  C ( $68^{\circ}$ - $104^{\circ}$  F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction with a device such as the Type 45-A pH Controller manufactured by Chemtrix, Inc., Hillsboro, Oregon 97123 or its equivalent, in conjunction with a metering pump and reservoir of 0.5 N acetic acid. If such a system is not available, the following manual procedure shall be employed.

7.13.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

7.13.2 The pH of the solution should be checked and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches  $5.0 \pm 0.2$ . The pH of the solution should be adjusted at 15-, 30-, and 60-min intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5 pH units.

7.13.3 The adjustment procedure should be continued for at least 6 hr.

7.13.4 If, at the end of the 24-hr extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to  $5.0 \pm 0.2$  and the extraction continued for an additional 4 hr, during which the pH should be adjusted at 1-hr intervals.

7.14 At the end of the extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = ml deionized water to be added

W = weight in g of solid charged to extractor

A = ml of 0.5 N acetic acid added during extraction

7.15 The material in the extractor should be separated into its component liquid and solid phases in the following manner.

7.15.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus (refer to Section 4.3 and 4.4).

7.15.2 Wet the filter with a small portion of the waste's or extraction mixture's liquid phase. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10 psi increments to 75 psi. Halt filtration when liquid flow stops.

7.16 The liquids resulting from Sections 7.5 and 7.15 should be combined. This combined liquid (or the waste itself if it has less than 0.5% solids, as noted in Section 7.8) is the extract and should be analyzed for the presence of any of the contaminants specified in Table 1 using the Analytical Procedures designated in Section 7.17.

7.17 The extract will be prepared and analyzed according to the analytical methods specified in Table 1. All of these analytical methods are included in this manual. The method of standard addition will be employed for all metal analyses.

NOTE: If the EP extract includes two phases, concentration of contaminants is determined by using a simple weighted average. For example: An EP extract contains 50 ml of oil and 1,000 ml of an aqueous phase. Contaminant concentrations are determined for each phase. The final contamination concentration is taken to be

$$\frac{(50)(\text{contaminant conc. in oil})}{1,050} + \frac{(1,000)(\text{contaminant conc. of aqueous phase})}{1,050}$$

7.18 The extract concentrations are compared to the maximum contamination limits listed in Table 1. If the extract concentrations are equal to or greater than the respective values, then the waste is considered to be EP toxic.<sup>1</sup>

<sup>1</sup>Chromium concentrations have to be interpreted differently. A waste containing chromium will be determined to be EP toxic if (1) the waste extract has an initial pH of less than 7 and contains more than 5 mg/l of hexavalent chromium in the resulting extract, or (2) the waste extract has an initial pH greater than 7 and a final pH greater than 7 and contains more than 5 mg/l of hexavalent chromium in the extract, or (3) the waste extract has an initial pH greater than 7 and a final pH less than 7 and contains more than 5 mg/l of total chromium, unless the chromium is trivalent. To determine whether the chromium is trivalent, the sample must be processed according to an alkaline digestion method (Method 3060) and analyzed for hexavalent chromium (Methods 7195, 7196, or 7197).

8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 All quality control measures suggested in the referenced analytical methods should be followed.

## 2.2 Mobility Procedures

Mobility procedures are used to determine the mobility of various components in a waste. Although these procedures are used to evaluate a waste, they are not to be confused with a hazardous characteristic as defined by the RCRA Regulations, Part 261.

METHOD 1410

MULTIPLE EXTRACTION PROCEDURE

This method is presently under development.

SECTION FOUR

SAMPLE WORKUP TECHNIQUES

4.1 Inorganic Techniques (beginning of 3000 series)

Methods appropriate for sample workup prior to analysis by inorganic techniques (6000 and 7000 series) are included on the following pages.

## METHOD 3010

### ACID DIGESTION PROCEDURE FOR FLAME ATOMIC ABSORPTION SPECTROSCOPY

#### 1.0 Scope and Application

1.1. This digestion procedure is approved for the preparation of aqueous samples, EP and mobility procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (AAS), for the metals listed below. The procedure is to be used when one is to determine the total amount of the metal in the sample.

1.2 Metals for which Method 3010 is the approved flame AAS procedure are:

Aluminum	Lead
Antimony	Magnesium
Barium	Manganese
Beryllium	Molybdenum
Cadmium	Nickel
Calcium	Potassium
Chromium	Sodium
Cobalt	Tin
Copper	Vanadium
Iron	Zinc

1.3 If a nonaqueous sample is not completely digested by this method and determination as to the total concentration of a metal in the entire sample is required, then the digestion methods described in Method 3030, 3040, or 3050 should be tried. Some wastes will require fusion techniques to completely release metals from inorganic matrices. The appropriate fusion method should be chosen from the literature and its applicability to the sample of interest proven by analyzing spiked samples and relevant standard reference materials.

1.4 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy, since hydrochloric acid can cause interferences during atomization.

#### 2.0 Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is heated to near dryness in a Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to near dryness, it is cooled and brought up in dilute hydrochloric acid.

### 3.0 Interferences

3.1 Interferences are discussed in the referring analytical method.

### 4.0 Apparatus and Materials

4.1 Griffin beakers of assorted sizes.

4.2 Qualitative filter paper or centrifugation equipment.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrochloric acid (1:1): Prepared from deionized distilled water (or equivalent) and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Aqueous wastewaters must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc.  $\text{HNO}_3$ . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc.  $\text{HNO}_3$ . Re-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. It should be noted that if a sample is allowed to go to dryness, low recoveries may result for tin and antimony.

7.2 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 a small quantity of 1:1 HCl (5 ml/100 ml of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with distilled water and when necessary filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute nitric acid. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

## 8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

## METHOD 3020

### ACID DIGESTION PROCEDURE FOR FURNACE ATOMIC ABSORPTION SPECTROSCOPY

#### 1.0 Scope and Application

1.1 This digestion procedure is approved for the preparation of aqueous samples, mobility procedure extracts, and certain nonaqueous wastes for analysis, by furnace atomic absorption spectroscopy (AAS), for the metals listed below. The procedure is to be used when one is to determine the total amount of the metal in the sample.

1.2 Metals for which Method 3020 is the approved furnace AAS procedure are:

Aluminum	Lead
Barium	Manganese
Beryllium	Molybdenum
Cadmium	Nickel
Chromium	Silver
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc

1.3 If a *nonaqueous* sample is not completely digested by this method and determination as to the total concentration of a metal in the entire sample is required, then the digestion methods described in Method 3030, 3040, or 3050 should be tried. Some wastes will require fusion techniques to completely release metals from inorganic matrices. The appropriate fusion method should be chosen from the literature and its applicability to the sample of interest proven by analyzing spiked samples and relevant standard reference materials.

#### 2.0 Summary of Method

2.1 A mixture of nitric acid and the material to be analyzed is heated to near dryness in a Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to near dryness, it is cooled and brought up in dilute nitric acid such that the final dilution contains 0.5% (v/v) HNO<sub>3</sub>.

#### 3.0 Interferences

3.1 Interferences are discussed in the referring analytical method.

## 2 / WORKUP TECHNIQUES - Inorganic

### 4.0 Apparatus and Materials

4.1 Griffin beakers of assorted sizes.

4.2 Qualitative filter paper or centrifugation equipment.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Aqueous wastewaters must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc.  $\text{HNO}_3$ . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc.  $\text{HNO}_3$ . Re-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. It should be noted that if a sample is allowed to go to dryness, low recoveries may result for tin and antimony.

7.2 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 a small quantity of  $\text{HNO}_3$  so that the final dilution contains 0.5% (v/v)  $\text{HNO}_3$ , and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with distilled water and when necessary filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute nitric acid. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

## 8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

## METHOD 3030

### ACID DIGESTION OF OILS, GREASES, OR WAXES

#### 1.0 Scope and Application

1.1 This digestion procedure is approved for the preparation of samples that contain substantial amounts of oils, greases, or waxes and that will be analyzed for the total concentration of the following metals: arsenic, cadmium, chromium, mercury, selenium, and silver. Since certain matrices may result in poor recovery, the method of standard addition shall be used.

#### 2.0 Summary of Method

2.1 A representative sample is placed in a Kjeldahl or similar flask and is subjected to digestion by sulfuric acid, nitric acid, and hydrogen peroxide. The digestate is diluted to volume and is ready for analysis.

#### 3.0 Interferences

3.1 Interferences are discussed in the referring analytical method.

#### 4.0 Apparatus and Materials

4.1 Ground-glass-stoppered 300-ml Kjeldahl flask (acid precleaned).

4.2 300-mm Allihn condenser filled to 50 mm with rashing rings or glass beads (acid precleaned).

4.3 6-mm glass bead (acid precleaned).

4.4 Heating mantle.

#### 5.0 Reagents

5.1 Concentrated nitric acid.

5.2 Concentrated sulfuric acid.

5.3 Concentrated hydrochloric acid.

5.4 30% hydrogen peroxide.

NOTE: The above reagents should be analyzed to determine the level of impurities. If impurities are detected, all analyses should be blank-corrected.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Samples shall be stored in an undiluted state at room temperature.

6.2 Samples should be processed and analyzed as soon as possible.

## 7.0 Procedure

7.1 Weigh out a 100-g representative sample of the waste or extract. Separate the phases if more than one is present, and weigh each phase. Weigh 2.0 g of the organic phase into the digestion or Kjeldahl flask. Add 10 ml  $\text{H}_2\text{SO}_4$  and a 6-mm glass bead. Swirl flask to mix the contents.

7.2 Approximately three-fourths of the neck of the Kjeldahl flask should be cooled by directing an air stream against the neck of the flask. If an Allihn condenser is employed, water will be used to cause refluxation and the air stream is not required.

7.3 Heat the flask gently and continue heating until dense white fumes appear and the solution boils. Cautiously add 1 ml  $\text{HNO}_3$  dropwise to oxidize the organic material. This may be done through the condenser. When the  $\text{HNO}_3$  has boiled off and dense white fumes reappear, repeat the treatment with an additional 1 ml of  $\text{HNO}_3$ . Continue the addition of  $\text{HNO}_3$  in 1-ml increments until the digestion mixture is no darker than a straw color, indicating that most of the organic matter has been oxidized.

7.4 Cool the flask slightly and add 0.5 ml (dropwise) of  $\text{H}_2\text{O}_2$ . Heat until dense white fumes appear, and while boiling, cautiously add 1 ml of  $\text{HNO}_3$  dropwise. When the  $\text{HNO}_3$  has boiled off and dense white fumes reappear, repeat the treatment with  $\text{H}_2\text{O}_2$  and  $\text{HNO}_3$  until the digestion mixture is colorless, at which time the organic material will be completely oxidized. Four treatments will usually suffice.

7.5 When oxidation is complete, allow the flask to cool, wash down the condenser with a small volume of distilled water (5 ml) and mix the contents. Continue heating until dense white fumes appear.

7.6 Cool. If a precipitate forms, add 2 ml of conc.  $\text{HCl}$  before diluting to remove the precipitate. If the precipitate persists, filter or centrifuge the solution to remove the precipitate, and proceed to determine As, Ba, Cd, Cr, Hg, Pb, and Se concentrations. Dilute to a total volume of 25 ml.  $\text{HCl}$  should not be added if Ag concentrations are to be determined.

7.7 The digestate as well as any aqueous phases that may have been present are analyzed for metal content by the appropriate method specified in this manual. Metal concentrations should be reported as the weighted average for both phases.

## 8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

## METHOD 3040

### DISSOLUTION PROCEDURE FOR OILS, GREASES, OR WAXES

#### 1.0 Scope and Application

1.1 Method 3040 is approved for the preparation of samples containing oils, greases, or waxes which will be analyzed for barium, cadmium, chromium, lead, and silver. While this method may also be applicable to the analysis of other metals in these matrices, further work is necessary to validate the method for other metals.

#### 2.0 Summary of Method

2.1 A representative sample is dissolved in an appropriate solvent (e.g., xylene or methyl isobutyl ketone). Organometallic standards are prepared using the same solvent, and the samples and standards are analyzed by atomic absorption spectroscopy (AAS) or inductively coupled argon plasma emission spectroscopy (ICP).

#### 3.0 Interferences

3.1 Diluted samples and diluted organometallic standards are often unstable. Once standards and samples are diluted they should be analyzed as soon as possible.

3.2 Solvent blanks should be used to thoroughly rinse nebulizers following aspiration of high concentration standards or samples.

3.3 Viscosity differences can result in different rates of sample introduction, so all analyses shall be performed by the method of standard addition. Peristaltic pumps often prove useful when analysis is performed by ICP.

#### 4.0 Apparatus

4.1 Volumetric glassware.

4.2 Balance.

4.3 Atomic Absorption Spectrometer having an auxiliary oxidant control and a mechanism for background correction.

4.4 Inductively Coupled Argon Plasma Emission Spectrometer system having a mechanism for background correction and interelement interference correction. A peristaltic pump is optional.

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### 5.0 Reagents

5.1 Methyl isobutyl ketone (MIBK).

5.2 Xylene.

5.3 Organometallic standards (two possible sources are Continental Oil Company, Ponca City, Oklahoma, and the U.S. Department of Commerce, National Bureau of Standards, Washington, D.C. 20234).

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples should be stored in an undiluted state at room temperature.

6.3 Solvent dissolution of samples should be performed as closely as possible to the time of analysis.

### 7.0 Procedure

7.1 Weigh out a 100-g representative sample of the waste or extract. Separate and weigh the phases if more than one phase is present.

7.2 Weigh an aliquot of the organic phase and dilute the aliquot in the appropriate solvent. Warming facilitates the subsampling of crude-type oils and greases and wax-type wastes. Xylene is usually the preferred solvent for longer-chain hydrocarbons and for most analyses performed by ICP. The longer-chain hydrocarbons usually require a minimum of a 1:10 dilution, while lighter oils may require only a 1:5 dilution if low detection limits are required.

7.3 When analyzing samples for alkali and alkaline earth metals, organometallic ionization suppressants (e.g., potassium cyclohexane butyrate) are suggested as a means of improving detection limits.<sup>1</sup> If ionization suppressants are employed, they must be added to both samples and standards.

7.4 All metals must be analyzed by the method of standard additions. Since the method of standard additions can account only for multiplicative interferences (matrix or physical interferences), the analytical program must account for additive interference (nonspecific adsorption and scattering in

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<sup>1</sup>The literature disagrees about the advantages of employing ionization suppressants; the analyst should use his/her own judgment whether to use these matrix modifiers.

AAS and nonspecific emission and interelement interference in ICP) by employing background correction.

7.5 Sample preparation for the method of standard additions can be performed on a weight or volume basis. Sample aliquots of viscous wastes should be weighed. Weigh identical amounts of the sample into three wide-mouth vials. Dilute the first vial such that the final concentration falls on the lower end of the linear portion of the calibration curve and significantly above the detection limit. Add sufficient standard to the second aliquot to increase the sample concentration by approximately 50%. Adjust the third sample concentration so that it is approximately twice that of the first. The second and third aliquots are then diluted to the same final volume as the first aliquot.

7.6 Set up and calibrate the analytical instrumentation according to the manufacturer's directions for nonaqueous samples.

7.7 Report data as the weighted average for all sample phases.

## 8.0 Quality Control

8.1 Procedural blanks (e.g., Conostan base oil or mineral oil plus reagents) should be carried through the complete sample preparation and analytical process on a routine basis. These blanks will be useful in detecting and determining the magnitude of any sample contamination.

8.2 Duplicate samples should be processed on a routine basis. These samples will be used to determine the precision of the method.

8.3 Samples and standards should be diluted as closely as possible to the time of analysis.

8.4 All analyses must be performed by the method of standard additions.

8.5 Data must be corrected for background absorption and emission and interelement interferences.

## METHOD 3050

### ACID DIGESTION OF SLUDGES

#### 1.0 Scope and Application

1.1 Method 3050 is an acid digestion procedure used to prepare sludge-type and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3050 may be analyzed by AAS or ICP for the following metals:

Antimony	Lead
Arsenic	Nickel
Barium	Selenium
Beryllium	Silver
Cadmium	Thallium
Chromium	Zinc
Copper	

1.2 Method 3050 may also be applicable to the analysis of other metals in sludge-type samples. However, prior to using this method for other metals, it must be evaluated using the specific metal and matrix.

#### 2.0 Summary of Method

2.1 A dried and pulverized sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace analysis of Sb or the flame analysis of Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, and Zn. Nitric acid is employed as the final reflux acid for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Ag, Tl, and Zn or the flame analysis of Ag and Tl.

#### 3.0 Interferences

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste. Nondestructive techniques such as neutron activation analysis may also be helpful in evaluating the applicability of this digestion method.

#### 4.0 Apparatus and Materials

4.1 125-ml conical Phillips' beakers.

4.2 Watch glasses.

- 4.3 Drying ovens that can be maintained at 30° C.
- 4.4 Thermometer that covers range of 0° to 200° C.
- 4.5 Whatman No. 42 filter paper or equivalent.

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.3 Concentrated hydrochloric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

5.4 Hydrogen peroxide (30%): Oxidant should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank corrected.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Weigh and transfer to a 125-ml conical Phillips' beaker a 1.0-g portion of sample which has been dried at 60° C, pulverized, and thoroughly mixed.

7.2 Add 10 ml of 1:1 nitric acid (HNO<sub>3</sub>), mix the slurry, and cover with a watch glass. Heat the sample at 95° C and reflux for 10 min. Allow the sample to cool, add 5 ml of conc. HNO<sub>3</sub>, replace the watch glass, and reflux for 30 min. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

7.3 After the second reflux step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide ( $H_2O_2$ ). Return the beaker to the hot plate for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

7.4 Continue to add 30%  $H_2O_2$  in 1-ml aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 ml 30%  $H_2O_2$ .)

7.5 If the sample is being prepared for the furnace analysis of Ag and Sb or direct aspiration analysis of Ag, Sb, Ba, Be, Cd, Cr, Cu, Pb, Ni, Tl, and Zn, add 5 ml of 1:1 HCl and 10 ml of Type II water, return the covered beaker to the hot plate, and heat for an additional 10 min. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 0.5% (v/v)  $HNO_3$  and is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Ba, Be, Cd, Cr, Cu, Pb, Ni, Se, Tl, and Zn, continue heating the acid-peroxide digestate until the volume has been reduced to approximately 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water (or centrifuge the sample). The diluted digestate solution contains approximately 2% (v/v)  $HNO_3$ . For analysis, withdraw aliquots of appropriate volume, add any required reagent or matrix modifier, and analyze by method of standard additions.

## 8.0 Quality Control

8.1 For each group of samples processed, procedural blanks (Type II water and reagents) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 10% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

8.4 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

## METHOD 3060

### ALKALINE DIGESTION

#### 1.0 Scope and Application

1.1 Method 3060 is used to determine the total concentration of hexavalent chromium in solid wastes.

#### 2.0 Summary of Method

2.1 This method uses a basic digestion of the waste sample to solubilize both water-insoluble and water-soluble hexavalent chromium compounds.

2.2 The sample is extracted with hot, 3% sodium carbonate-2% sodium hydroxide solution to dissolve all Cr(VI) and to protect it from reduction to trivalent chromium.

#### 3.0 Interferences

3.1 Wastes containing high amounts of buffering capability may require additional digestion solution (see section 5.5) to properly digest the sample.

#### 4.0 Apparatus

4.1 Beakers: borosilicate, 600-ml, with watch glass covers.

4.2 Filtration apparatus: pressure 75 psi, with 0.45- $\mu$  filter.

4.3 Volumetric flasks: 1-liter.

4.4 Hot Plate: 120-140° C.

4.5 Pipettes: assorted sizes, as necessary.

#### 5.0 Reagents

5.1 Nitric acid: HNO<sub>3</sub>, concentrated, analytical reagent grade or spectrograde quality.

5.2 Sodium carbonate: Na<sub>2</sub>CO<sub>3</sub>, anhydrous, analytical reagent grade.

5.3 Sodium hydroxide: NaOH, analytical reagent grade.

5.4 Potassium dichromate: K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, analytical reagent grade.

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5.5 Digestion solution: Dissolve 20.0 g sodium hydroxide and 30.0 g sodium carbonate in deionized distilled water in a 1-liter volumetric flask and dilute to the mark. Store the solution in a tightly capped polyethylene bottle and prepare fresh monthly.

5.6 Potassium dichromate spiking solution (1 ml = 1 mg Cr): Dissolve 28.29 g of dried potassium dichromate in deionized distilled water in a 1-liter volumetric flask and dilute to the mark.

### 6.0 Sample Handling and Preservation

6.1 To retard the chemical activity of hexavalent chromium, the sample and digestate should be stored at 4° C until analyzed.

6.2 Since the chemistry of hexavalent chromium is not fully understood, all samples should be analyzed as soon as possible.

### 7.0 Procedure

7.1 Place 100 g of the waste into a 600-ml beaker.

7.2 Add 400 ml of digestion solution (see section 5.5). Cover the beaker with the watch glass and heat it to near boiling on a hot plate with constant mixing for 30 to 45 min. Do not allow to go to dryness, as hexavalent chromium may be lost due to side reactions in the waste.

7.3 Cool the solution and transfer it quantitatively to the filtration apparatus with deionized distilled water rinses and filter. Rinse the inside of the filter flask and filter pad with deionized distilled water and transfer the filtrate and the rinses to a 1-liter volumetric flask.

7.4 If the sample will not be immediately analyzed, it should be stored at a high pH. Just prior to analysis, place a magnetic stirring bar into the flask, place the flask on a stirrer and, with constant stirring, slowly add concentrated nitric acid to the flask in small aliquots. Bring the pH of the solution to between 7 and 8. Caution: carbon dioxide will be evolved.

7.5 Remove the stirring bar and rinse the bar into the flask. Dilute the contents of the flask to the mark with deionized distilled water.

7.6 Select one of the methods given for determining the concentration of hexavalent chromium (7195, 7196, or 7197) and determine the amount of hexavalent chromium in the digestate immediately.

7.7 Calculate the amount of hexavalent chromium in the sample in mg/kg. A sample calculation could be as follows:

A digested 100-g waste sample was found to contain 12.0 mg/l in the final digestate, or 12.0 mg/100 g of hexavalent chromium in the waste. This material would be considered hazardous since it could result in the release of more than 5 mg/l of hexavalent chromium in an EP leachate (i.e., 12 mg hexavalent chromium in the final EP leachate volume of 2 liters would equal 6 mg/l).

## 8.0 Quality Control

8.1 For every sample matrix analyzed, verification is required to determine that neither a reducing condition nor chemical interference affecting the digestion is present. This must be accomplished by analyzing a second 100-g aliquot of the waste that has been spiked with Cr(VI) (see section 5.6). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 0.10 mg/g. To verify the absence of an interference, the spike recovery should be between 85% and 115%. If the result of verification indicates a suppressive interference, the analysis will not be considered to be valid, and further guidance should be obtained prior to basing any decisions on the data obtained.

#### 4.2 Organic Techniques (end of 3000 series)

Methods appropriate for sample workup prior to analysis by organic techniques (8000 series) are included on the following pages.

## METHOD 3510

### SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

#### 1.0 Scope and Application

1.1 Method 3510 is designed to quantitatively extract nonvolatile and semivolatile organic compounds from liquid samples using standard separatory funnel techniques. The sample and extracting solvent must be immiscible to yield recovery of target compounds. Subsequent cleanup and detection methods are described in the organic analytical method that will be used to analyze the extract.

#### 2.0 Summary of Method

2.1 Samples are adjusted to a specified extraction pH and extracted with the appropriate solvent. Methylene chloride should be employed when a solvent is not specified. The extraction pH and solvent to be used are listed in each referring analytical method. Samples are extracted three times, and the combined extracts are dried with anhydrous sodium sulfate and concentrated in a Kuderna-Danish apparatus.

#### 3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the referring analytical methods.

#### 4.0 Apparatus

4.1 Separatory funnel: 2-liter, with Teflon stopcock.

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with coarse frit.

4.3 Kuderna-Danish (K-D) apparatus.

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

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4.6 pH indicator paper with a pH range including the desired extraction pH.

### 5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical method that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used, and it should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Sodium hydroxide: (ACS) 10 N in distilled water.

5.5 Sulfuric acid: (1:1) Mix equal volumes of concentrated H<sub>2</sub>SO<sub>4</sub> (ACS) with distilled water.

5.6 Distilled water.

5.7 Methylene chloride: Pesticide quality or equivalent.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

### 7.0 Procedure

7.1 Transfer 1 liter of sample to the separatory funnel. If less than 1 liter of sample is available or if high concentrations are anticipated, use a smaller volume of sample and, if necessary, add laboratory distilled water until sample volume is suitable for extraction.

7.2 Adjust the pH of the sample to that indicated in the referring method.

7.3 Add 60 ml of the appropriate extraction solvent, as indicated in the referring method.

7.4 Seal and shake the separatory funnel for 60 sec with periodic venting to release vapor pressure.

7.5 Allow the phases to separate for a minimum of 10 min. 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.

7.6 Collect the extract and then repeat the extraction two more times using fresh portions of solvent.

7.7 Combine the three extracts and appropriately discard the now extracted waste, if no further extractions are to be performed.

7.8 Dry the extract by passing it through a column of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish evaporative concentrator equipped with a 10-ml collection ampule.

7.9 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.10 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

## 8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 By fortifying distilled water or another liquid similar to the sample matrix, the analyst should demonstrate that the compound(s) of interest are being quantitatively recovered before applying this method to actual samples.

## METHOD 3520

### CONTINUOUS LIQUID-LIQUID EXTRACTION

#### 1.0 Scope and Application

1.1 Method 3520 is designed to quantitatively extract nonpurgeable organic compounds from liquid samples using a continuous extraction apparatus. This method is available as an alternative to Method 3510, which is a separatory funnel extraction procedure. Method 3520 is advantageous compared to standard separatory funnel techniques because it minimizes emulsion formation. The sample and extracting solvent must be immiscible to yield recovery of target compounds. Subsequent cleanup and detection are described in referring analytical methods.

1.2 Method 3520 is designed for extraction solvents with greater density than the sample. Continuous extraction devices are available for extraction solvents that are less dense than the sample. The analyst must demonstrate the effectiveness of any such automatic extraction device before employing it in sample extraction.

#### 2.0 Summary of Method

2.1 The sample is placed into the continuous extraction apparatus, adjusted to the proper extraction pH and extracted with the appropriate solvent. Methylene chloride should be employed when a solvent is not specified. The extraction pH and solvent to be used are listed in the quantification method. Samples are extracted for 16 hr; the extract is collected, dried with anhydrous sodium sulfate, and concentrated with a Kuderna-Danish apparatus. In some cases, the sample pH is adjusted after the first extraction, and continuous extraction is carried out for 16 hr to recover an additional class of compound.

#### 3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organical analytical method that will be used to analyze the sample.

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### 4.0 Apparatus and Materials

4.1 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass #LG-6915; or equivalent).

4.2 Drying column: 20-mm I.D. Pyrex chromatographic column with coarse frit.

4.3 Kuderna-Danish (K-D) apparatus.

4.4 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.6 pH indicator paper with a pH range that includes the desired extraction pH.

4.7 Rheostat controlled heating mantle.

### 5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical method that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at  $400^\circ$  C for 4 hr in a shallow tray).

5.4 Sodium hydroxide: (ACS) 10 N in distilled water.

5.5 Sulfuric acid: (1:1) Mix equal volumes of concentrated  $H_2SO_4$  (ACS) with distilled water.

5.6 Distilled water.

5.7 Methylene chloride: Pesticide quality or equivalent.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

## 7.0 Procedure

7.1 Refer to Figure 1 to aid in understanding the procedures described in Sections 7.2-7.6 for setting up the continuous extractor. The analyst is reminded that the following steps apply to sample/solvent systems where the solvent is more dense than the sample.

7.2 Place 150 ml of extracting solvent in the extractor and 350 ml of extracting solvent in the 500-ml distilling flask. Add several boiling chips to the distilling flask.

7.3 Measure out 1 liter of sample to be extracted. If less than 1 liter of sample is available or if high concentrations are anticipated, use a smaller volume of sample and, if necessary, add laboratory distilled water to bring the sample volume to 1 liter. Adjust the sample to the proper extraction pH, add surrogate standards, and add the sample to the extraction apparatus.

7.4 Add enough solvent to the extraction device to bring the sample level above the U-tube connector. Using the controlling rod, balance the distilling rate from the 500-ml distilling flask with the return flow through the U-tube connector.

7.5 Turn on the cooling water and the heating mantle and extract the sample for 16 hr.

7.6 Let the system cool and remove the extract contained in the 500-ml distilling flask.

7.7 If an additional extraction is to be performed, adjust the sample pH accordingly. Attach a 500-ml distilling flask containing 350 ml of extracting solvent, add several boiling chips, and proceed from step 7.4.

7.8 Dry the extract by passing it through a column of anhydrous sodium sulfate. Collect the dried extract in a Kuderna-Danish evaporative concentrator equipped with a 10-ml collection ampule.

7.9 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

7.10 Rinse the K-D apparatus with a small volume of solvent. Adjust sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

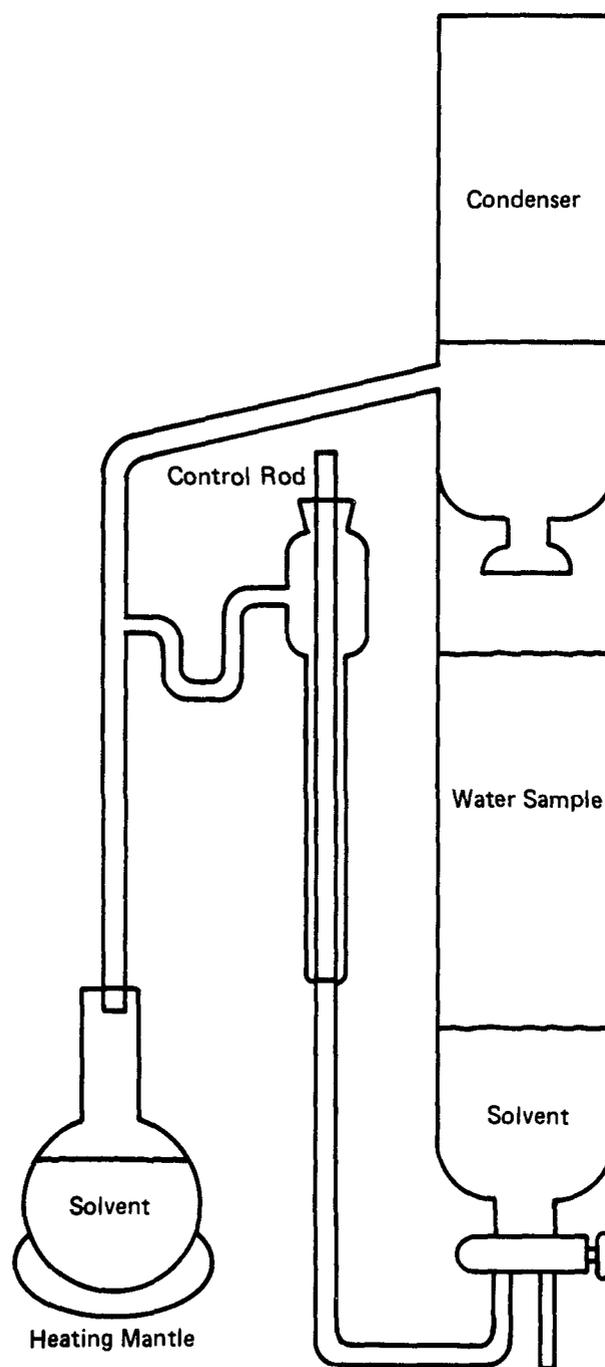


Figure 1. Continuous liquid-liquid extractor.

## 8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 By fortifying distilled water or another liquid similar to the sample matrix, the analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

## METHOD 3530

### ACID-BASE CLEANUP EXTRACTION

#### 1.0 Scope and Applications

1.1 Method 3530 is a sample cleanup procedure to be used when interferences prevent direct chromatographic measurement of the compound being analyzed for. The method makes use of the differential solubility of the compounds of interest and the interfering species.

#### 2.0 Summary of Method

2.1 Interferences are removed by a series of liquid-liquid extractions using a specified pH/solvent system.

#### 3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined for this method may be necessary for reagent purification.

#### 4.0 Apparatus and Materials

4.1 125-ml separatory funnel with Teflon stopcock.

4.2 Kuderna-Danish (K-D) apparatus equipped with a three-ball Snyder column.

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.4 Drying column: 20-mm I.D. Pyrex chromatographic column with coarse frit.

4.5 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^{\circ}$  C). The bath should be used in a hood.

4.6 pH indicator paper with a pH range including the desired sample pH.

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### 5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical method that will be used to analyze the extract following cleanup. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Sodium hydroxide: (ACS) 10 N in distilled water.

5.5 Sulfuric acid: (1:1) Mix equal volumes of concentrated H<sub>2</sub>SO<sub>4</sub> (ACS) with distilled water.

5.6 Distilled water.

5.7 Methylene chloride: Pesticide quality or equivalent.

### 6.0 Sample Collection, Preservation and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation and handling.

### 7.0 Procedure

7.1 Place 10 ml of the extract or organic liquid waste to be cleaned up into the separatory funnel.

7.2 Add 20 ml of the solvent indicated in Table 1.

7.3 Add 20 ml of distilled water and adjust the pH to 12-13 with sodium hydroxide. Partition the sample into the solvent and aqueous phases by shaking the funnel for 1 min with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the 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.

7.4 Separate the aqueous phase and transfer to a 125-ml Erlenmeyer flask.

TABLE 1. APPROPRIATE CLEANUP SOLVENT AND STEP 7.6 PHASE FOR INDIVIDUAL COMPOUNDS

Compound being analyzed for	Solvent	Step 7.6 phase
Benzo(a)anthracene	Dichloromethane	Solvent
Benzo(a)pyrene	Dichloromethane	Solvent
Benzotrichloride	Dichloromethane	Solvent
Benzyl chloride	Dichloromethane	Solvent
Benzo(b)fluoranthene	Dichloromethane	Solvent
Chlordane	Dichloromethane	Solvent
Chlorinated dibenzodioxins	Dichloromethane	Solvent
2-Chlorophenol	Dichloromethane	Aqueous
Chrysene	Dichloromethane	Solvent
Creosote <sup>a</sup>	Dichloromethane	Solvent
Cresol(s)	Dichloromethane	Aqueous
Cresylic acid(s)	Dichloromethane	Aqueous
Dichlorobenzene(s)	Dichloromethane	Solvent
Dichlorophenoxy-acetic acid	Ethyl ether	Aqueous
Dichloropropanol	Dichloromethane	Solvent
2,4-Dimethylphenol	Dichloromethane	Aqueous
Dinitrobenzene	Dichloromethane	Solvent
4,6-Dinitro-o-cresol	Dichloromethane	Aqueous
2,4-Dinitrotoluene	Dichloromethane	Solvent
Endrin	Dichloromethane	Solvent
Heptachlor	Dichloromethane	Solvent
Hexachlorobenzene	Dichloromethane	Solvent
Hexachlorobutadiene	Dichloromethane	Solvent
Hexachloroethane	Dichloromethane	Solvent
Hexachlorocyclopentadiene	Dichloromethane	Solvent
Lindane	Dichloromethane	Solvent
Maleic anhydride	Dichloromethane	Solvent
Methomyl	Dichloromethane	Solvent
Naphthalene	Dichloromethane	Solvent
Naphthoquinone	Dichloromethane	Solvent
Nitrobenzene	Dichloromethane	Solvent
4-Nitrophenol	Dichloromethane	Aqueous
Pentachlorophenol	Dichloromethane	Aqueous
Phenol	Dichloromethane	Aqueous
Phorate	Dichloromethane	Solvent
Phosphorodithioic acid esters	Dichloromethane	Solvent
Phthalic anhydride	Dichloromethane	Solvent
2-Picoline	Dichloromethane	Solvent
Pyridine	Dichloromethane	Solvent
Tetrachlorobenzene(s)	Dichloromethane	Solvent
Tetrachlorophenol	Dichloromethane	Aqueous
Toluenediamine	Dichloromethane	Solvent
Toxaphene	Dichloromethane	Solvent
Trichlorophenol(s)	Dichloromethane	Aqueous
2,4,5-TP (Silvex)	Ethyl ether	Aqueous

<sup>a</sup>Phenolic compounds will partition into the aqueous phase while polynuclear hydrocarbon components will partition into dichloromethane.

#### 4 / WORKUP TECHNIQUES - Organic

7.5 Reextract the solvent layer twice more with 20-ml portions of distilled water at pH 12-13. Combine aqueous extract.

7.6 At this point the species being analyzed for will be in either the organic or the aqueous phase (see Table 1). If the species is in the aqueous phase, discard the organic phase and proceed to step 7.7. If the species is in the organic phase, discard the aqueous phase and proceed to step 7.12.

7.7 Transfer the aqueous phase to a clean separatory funnel.

7.8 Adjust the aqueous layer to a pH of 1-2 with sulfuric acid.

7.9 Add 20 ml of solvent to the funnel and shake for 2 min. Allow the solvent to separate from the aqueous phase and collect the solvent in a 100-ml Erlenmeyer flask.

7.10 Add a second 20-ml volume of solvent to the separatory funnel and reextract at pH 1-2 a second time, combining the extracts in the Erlenmeyer flask.

7.11 Perform a third extraction in the same manner.

7.12 Pour the combined organic extracts through a drying column containing 10 cm of anhydrous sodium sulfate, and collect it in a Kuderna-Danish (K-D) flask equipped with a 10-ml concentrator tube. Rinse the Erlenmeyer flask and column with 20 ml of solvent to complete the quantitative transfer.

7.13 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml of solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask is bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.14 If the appropriate analytical solvent is the same as that used for the above extraction, transfer the extract to a 10-ml volumetric flask and adjust the volume to 10 ml. If a different solvent is to be used for sample measurement, proceed as in step 7.15.

7.15 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 the extraction solvent. Note: 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 of the solvent 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 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 2.5 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Add an additional 2 ml of the extraction solvent 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 min while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of the extraction solvent. Transfer to a 10-ml volumetric flask and adjust the extract volume to 10 ml. Store in refrigerator, 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 further cleanup, proceed as appropriate.

## 8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

## METHOD 3540

### SOXHLET EXTRACTION

#### 1.0 Scope and Application

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils and sludges. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

#### 2.0 Summary of Method

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. Methylene chloride should be employed when a solvent is not specified. The extract is then dried and concentrated, and either cleaned up further or analyzed directly by the appropriate measurement technique.

#### 3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

#### 4.0 Apparatus and Materials

4.1 Soxhlet extractor: 40-mm I.D., with 500-ml round-bottom flask.

4.2 Kuderna-Danish apparatus with three-ball Snyder column.

4.3 Chromatographic column: Pyrex, 20-mm I.D., approximately 400 mm long, with coarse-fritted plate on bottom and an appropriate packing medium.

4.4 Glass or paper thimble or glass wool to retain sample in Soxhlet extraction device. Should drain freely and may require purification before use.

4.5 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.6 Rheostat controlled heating mantle.

## 2 / WORKUP TECHNIQUES - Organic

### 5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical methods that will be used to analyze the extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Soil samples: Soil samples shall be extracted using either of the following solvent systems.

5.4.1 Toluene/Methanol, 10:1 v/v ACS reagent grade only.

5.4.2 Acetone/Hexane, 1:1 v/v ACS reagent grade only.

5.5 Methylene chloride: Pesticide quality or equivalent.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

### 7.0 Procedure

7.1 Blend 10 g of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. The use of a glass wool plug above and below the sample is also acceptable.

7.2 Place 300 ml of the extraction solvent into a 500-ml round-bottom flask containing a boiling stone. Attach the flask to the extractor, and extract the solids for 16 hr.

7.3 Allow the extract to cool after the extraction is complete. Rinse the condenser with the extraction solvent and drain the Soxhlet apparatus into the collecting round-bottom flask. Filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flask fitted with a 10-ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

## 8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

## METHOD 3550

### SONICATION EXTRACTION

#### 1.0 Scope and Application

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils and sludges. The sonication process ensures intimate contact of the sample matrix with the extraction solvent. Subsequent cleanup and detection are described in the organic analytical method that will be used to analyze the extract.

#### 2.0 Summary of Method

2.1 A weighed sample of the solid waste is ground, mixed with the extraction medium, then dispersed into the solvent using sonication. The extract is then dried with anhydrous sodium sulfate and concentrated with Kuderna-Danish apparatus. The resulting solution may then be cleaned up further or analyzed directly using the appropriate technique.

#### 3.0 Interferences

3.1 A procedural blank should be performed for the compounds of interest prior to the use of this method. The level of interferences must be below the method detection limit before this method is performed on actual samples.

3.2 More extensive procedures than those outlined in this method may be necessary for reagent purification.

3.3 Procedures for the removal of interfering compounds coextracted with target compounds are described in the organic analytical method that will be used to analyze the extract.

#### 4.0 Apparatus and Materials

4.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples except gummy, fibrous, or oily materials.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicators, or an equivalent brand and model, are recommended: Sonifer/cell disruptor, model W-350, Ultrasonics Inc., or

## 2 / WORKUP TECHNIQUES - Organic

Sonic dismembrator, model 300, Fisher Scientific Co., Catalog Number 15-338-40.

4.3 Kuderna-Danish apparatus with three-ball Snyder column.

4.4 Chromatographic column: Pyrex, 20-mm I.D., approximately 400-mm long, with coarse-fritted plate on bottom.

4.5 Rheostat-controlled heating mantle.

### 5.0 Reagents

5.1 The specific reagents to be employed in this method may be listed under the organic analytical method that will be used to analyze this extract. Check analytical method for specific extraction reagent. If a specific extracting reagent is not listed for the compound(s) of interest, methylene chloride shall be used.

5.2 The solvent of choice should be appropriate for the method of measurement to be used and should give an analyte-to-solvent partition coefficient of at least 1 to 1000.

5.3 Sodium sulfate: (ACS) Granular anhydrous (purified by heating at 400° C for 4 hr in a shallow tray).

5.4 Sodium hydroxide: (ACS) 10 N in distilled water.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Adhere to those procedures specified in the referring analytical methods for collection, preservation, and handling.

### 7.0 Procedure

7.1 Grind or otherwise subdivide the waste, so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Weigh 10.0 g of suitably dispersed material into a 75-ml glass flask, and add 30 ml of an appropriate solvent. Sonicate with agitation for approximately 15 min. Filter the resulting suspension. Reextract the solid residue with an additional 30-ml portion of solvent. Repeat the extraction a third time so as to sonicate for a total of 45 min.

7.3 After the extraction is complete, filter the extract and dry it by passing it through a 4-in. column of sodium sulfate which has been washed

with the extracting solvent. Collect the dried extract in a 500-ml Kuderna-Danish (K-D) flash fitted with a 10-ml graduated concentrator tube and a three-ball Snyder column. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent.

7.4 Add 1 or 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml solvent to the top. Place the K-D apparatus on a steam or hot water bath so that the concentrator tube and the entire lower rounded surface of the flask are bathed in hot water or vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Transfer to a 10-ml volumetric flask and adjust the volume to 10 ml.

7.5 Rinse the K-D apparatus with a small volume of solvent. Adjust the sample volume to 10.0 ml with the solvent to be used in instrumental analysis. Proceed with analysis and cleanup if necessary.

## 8.0 Quality Control

8.1 Comprehensive quality control procedures are specified for each target compound in the referring analytical method.

8.2 The analyst should demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples.

## SECTION FIVE

### SAMPLE INTRODUCTION TECHNIQUES

The methods on the following pages (5000 series) are appropriate for sample introduction into instrumentation specified by organic analytical techniques (8000 series).

## METHOD 5020

### HEADSPACE METHOD

#### 1.0 Scope and Application

1.1 Method 5020 is a static headspace technique for extracting volatile organic compounds in pastes, solids, and liquids. It is a simple method that allows large numbers of samples to be analyzed in a relatively short period of time. Because of the large variability and complicated matrices of waste samples in the solid and paste forms, detection limits for this method may vary widely among samples. The method works best for compounds with boiling points of less than 125° C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

#### 2.0 Summary of Method

The sample is collected in sealed glass containers and allowed to equilibrate at 90° C. A sample of the headspace gas is withdrawn with a gas-tight syringe for analysis by the appropriate gas chromatographic method (8010, 8015, 8020, or 8030).

#### 3.0 Interferences

Refer to Methods 8010, 8015, 8020, or 8030.

#### 4.0 Apparatus and Materials

4.1 Gas-tight syringe: 5-cc with chromatographic needles.

4.2 Headspace standard solutions: Prepare according to procedures in 8010, 8015, 8020, or 8030 at 50 ng/μl and 250 ng/μl concentrations.

4.3 Vials: 125-ml Hypo-Vials (Pierce Chemical Co., #12995, or equivalent).

4.4 Septa: Tuf-Bond (Pierce #12720, or equivalent).

4.5 Seals: Aluminum (Pierce #13214, or equivalent).

## 2 / SAMPLE INTRODUCTION TECHNIQUES

4.6 Crimper: Hand (Pierce #13212, or equivalent).

### 5.0 Reagents

5.1 Refer to Methods 8010, 8015, 8020, or 8030.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Methods 8010, 8015, 8020, or 8030.

### 7.0 Procedure

7.1 Place 10.0 g each of the well-mixed waste sample into three separate 125-ml septum seal vials.

7.2 Dose one sample vial through the septum with 200  $\mu$ l of a 50-ng/ $\mu$ l methanolic standard of the compounds of interest. Label this "1-ppm spike."

7.3 Dose a separate (empty) 125-ml septum seal vial with 200  $\mu$ l of the 50 ng/ $\mu$ l standard methanol solution. Label this "1-ppm standard."

7.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90° C water bath for 1 hr. Store the remaining sample vial at 4.0° C for possible future analysis.

7.5 While maintaining the vials at 90° C, withdraw 2 ml of the headspace gas with a gas-tight syringe and analyze by injecting into a GC, operating under the appropriate conditions for the GC measurement method being used (8010, 8015, 8020, or 8030).

7.6 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2x the background. Record retention times (RT) and peak areas of compounds of interest.

7.7 Analyze the 1-ppm spiked sample in the same manner. Record RT's and peak areas.

7.8 Analyze the undosed sample as in Section 7.7.

### 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

## 9.0 References

1. Hachenberg, H. and Schmidt, A. 1979. Gas chromatographic headspace analysis. Philadelphia: Hayden & Sons Inc.
2. Friant, S.L. and Suffet, I.H. 1979. Interactive effects of temperature, salt concentration, and pH on headspace analysis for isolating volatile trace organics in aqueous environmental samples. Anal. Chem. 51:2167-2172.

## METHOD 5030

### PURGE-AND-TRAP METHOD

#### 1.0 Scope and Application

1.1 Method 5030 is used to determine the concentration of volatile organic compounds in a variety of liquid and solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, groundwater, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 For highly volatile matrices, direct injection preceded by dilution should be used to prevent gross contamination of the instrumentation. For pastes, dilution of the sample until it becomes free-flowing is used to ensure adequate interfacial area. The success of this method also depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

1.4 Method 5030 is based upon a purge-and-trap, gas chromatographic procedure.

1.5 This method is recommended for use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs and skilled in the interpretation of chromatograms.

#### 2.0 Summary of Method

2.1 A portion of solid waste is dispersed in polyethylene glycol (PEG) or distilled-in-glass methanol to dissolve the volatile organic constituents. A portion of the PEG or methanol solution is combined with water in a specially designed purging chamber. For liquid and some semiliquid samples, PEG or methanolic extraction will not be necessary. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. (SPECIAL NOTE: For Methods 8020 and 8030, drying of the trap for 4 min under helium flow is required. See Figure 5 for configuration.) The gas chromatographic column is heated to elute the components which are detected by the appropriate detector (Methods 8010, 8020, 8030).

### 3.0 Interferences

3.1 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.3.

3.2 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 contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.4 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water (PEG or methanol solution) to check for cross contamination. After each use, the purging chamber is cleaned as described in Section 7.12. The trap and other parts of the system are also subject to contamination; therefore, frequent additional bakeout and purging of the entire system may be required.

### 4.0 Apparatus and Materials

4.1 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are commercially available.

4.1.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.1.2 The sorbent trap consists of a 1/8-in. O.D. (0.105-in. I.D.) x 25-cm-long stainless steel tube packed with the appropriate absorbents as described in Table 1 (see Figures 2 and 3).

4.1.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec.

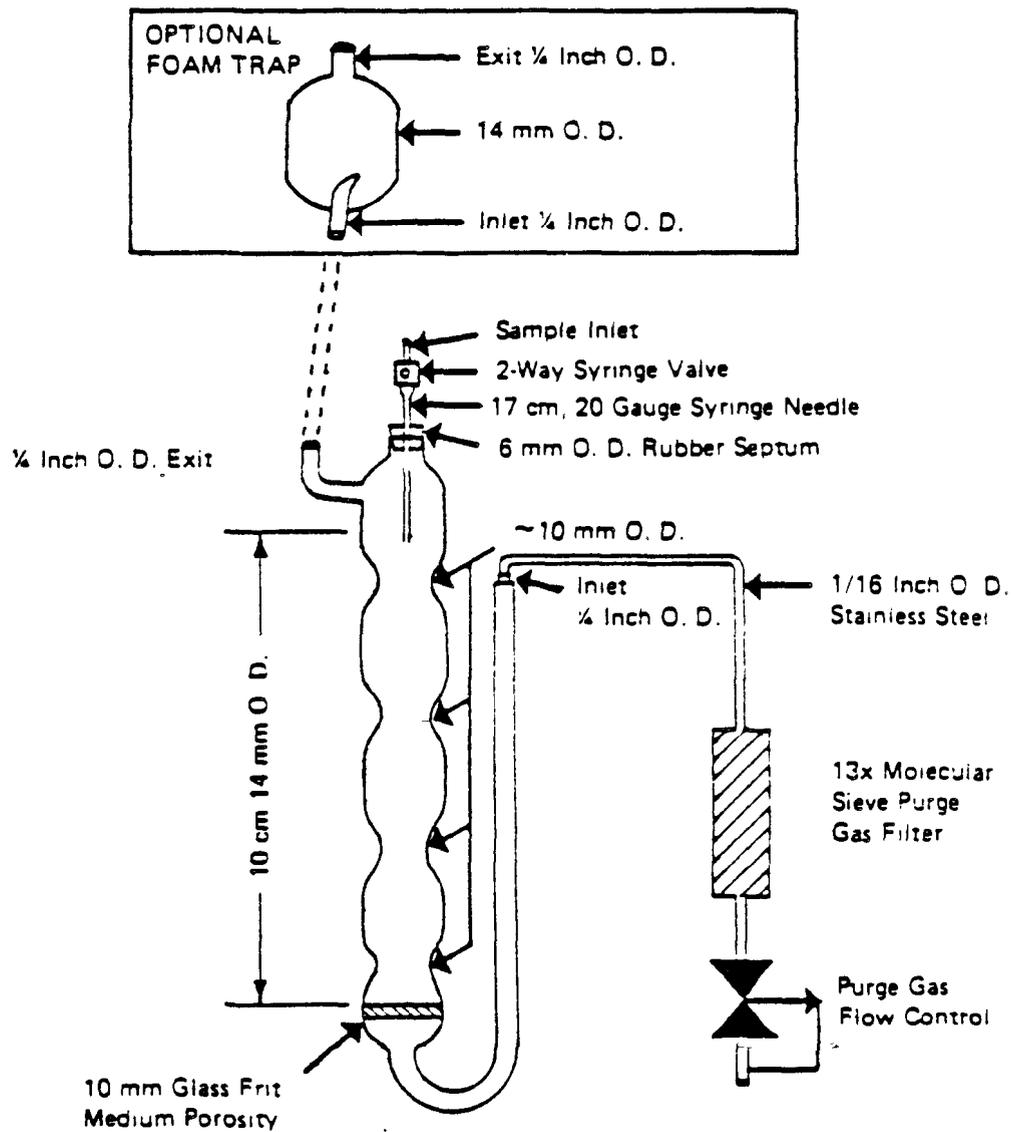


Figure 1. Purging chamber.

TABLE 1. PURGE-AND-TRAP PARAMETERS

	Analysis method <sup>a</sup>			
	8010	8015	8020	8030
Purge Gas	Nitrogen or Helium	Helium	Nitrogen or Helium	Helium
Purge Gas Flow Rate (ml/min)	40	40	40	20 $\pm$ 1
Purge Time (min)	11.0	12.0	12.0	30.0
Purge Temperature	Ambient	Ambient	Ambient	85° C
Desorb Temperature (°C)	180°	180°	180°	100°
Sorbents to be used in packing tube	A	B	B	B

<sup>a</sup>Measurement method to be employed for identification and quantification.

KEY: A = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

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

Coconut charcoal, 6/10 mesh, Barnaby Chaney C.A. - 580-26 lot #M-2649 or equivalent.

Refer to Figure 2 for column packing.

B = Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene oxide).

Three percent OV-1 on Chromosorb-W 60/80 mesh (optional).

Refer to Figure 3 for column packing.

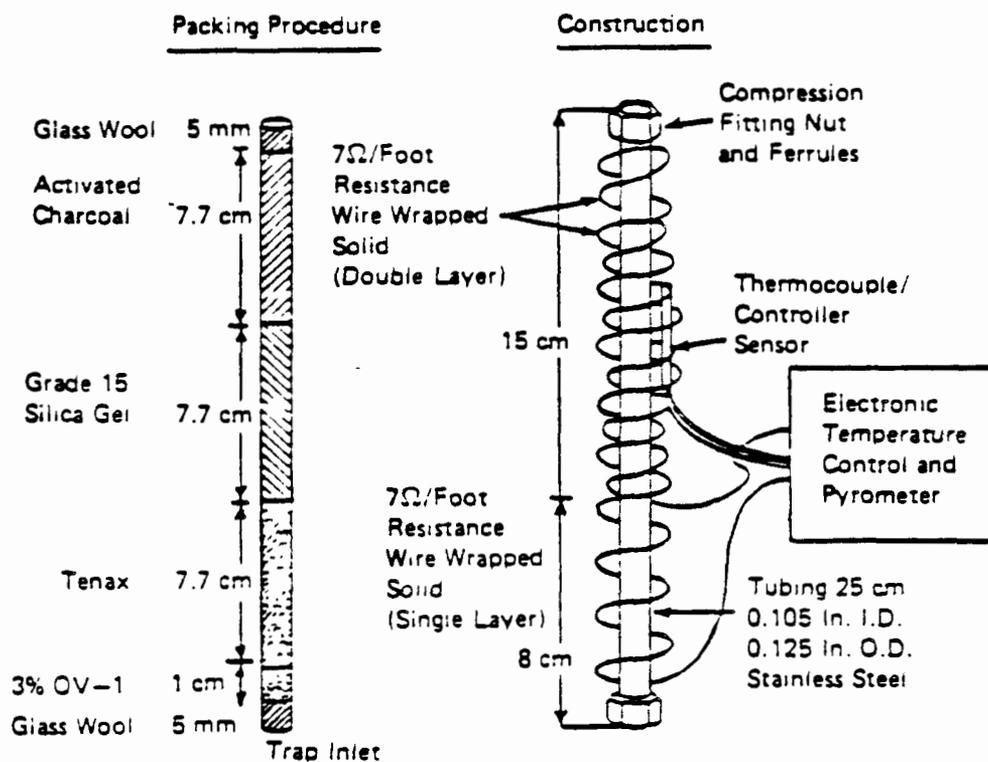


Figure 2. Trap packings and construction for Method 8010.

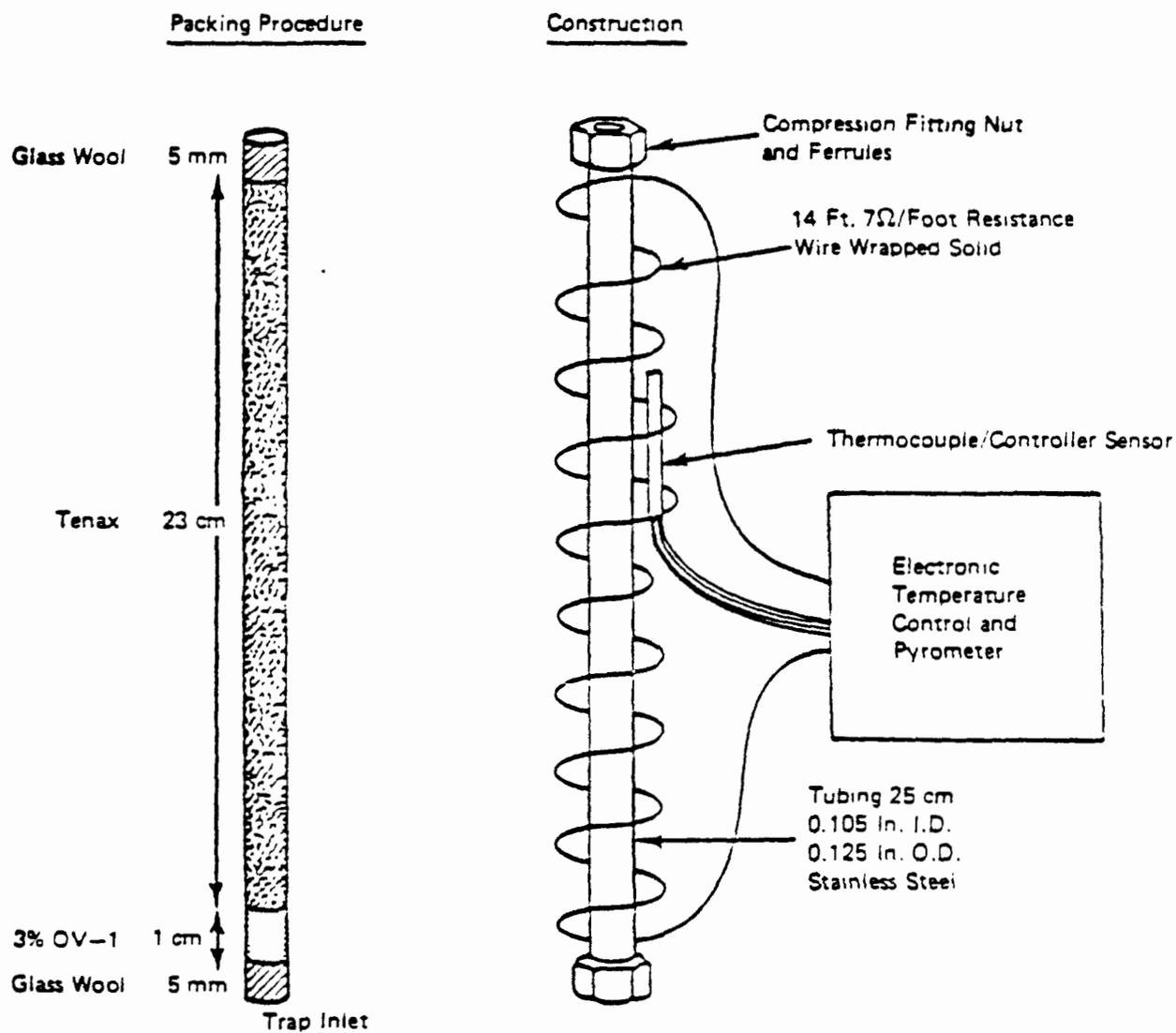


Figure 3. Trap packing and construction for Methods 8020 and 8030.

SECTION SIX

MULTIELEMENT INORGANIC ANALYTICAL METHODS

Methods appropriate for multielement inorganic analysis of samples (6000 series) are included on the following pages.

SECTION SEVEN

INORGANIC ANALYTICAL METHODS

Methods appropriate for inorganic analysis (7000 series) for specific elements of interest are included on the following pages.

4.1.4 The purge-and-trap device may be assembled as a separate unit or be coupled to a gas chromatograph as illustrated in Figures 4 through 6.

4.2 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.3 Micro syringes: 10  $\mu$ l, 25  $\mu$ l, 100  $\mu$ l, 250  $\mu$ l, 500  $\mu$ l, and 1,000  $\mu$ l. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.4 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation (Kimble #45212 or equivalent).

4.5 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.6 Syringe valve: 2-way, with Luer ends (2 each; Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting or equivalent).

4.7 Syringe: 5-ml, gas-tight with shutoff valve.

4.8 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.9 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.10 Rotary evaporator: Equipped with Teflon-coated seals (Buchi Rotavapor R-110 or equivalent).

4.11 Vacuum pump: Mechanical, two-stage.

## 5.0 Reagents

5.1 Trap materials (see Table 1 and Figures 2 and 3 for configuration).

5.1.1 2,6-Diphenylene oxide polymer: 60/80 mesh Tenax, chromatographic grade or equivalent.

5.1.2 Methyl silicone packing: 3% OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.1.3 Silica gel, Davison Chemical (35/60 mesh), grade 15 or equivalent.

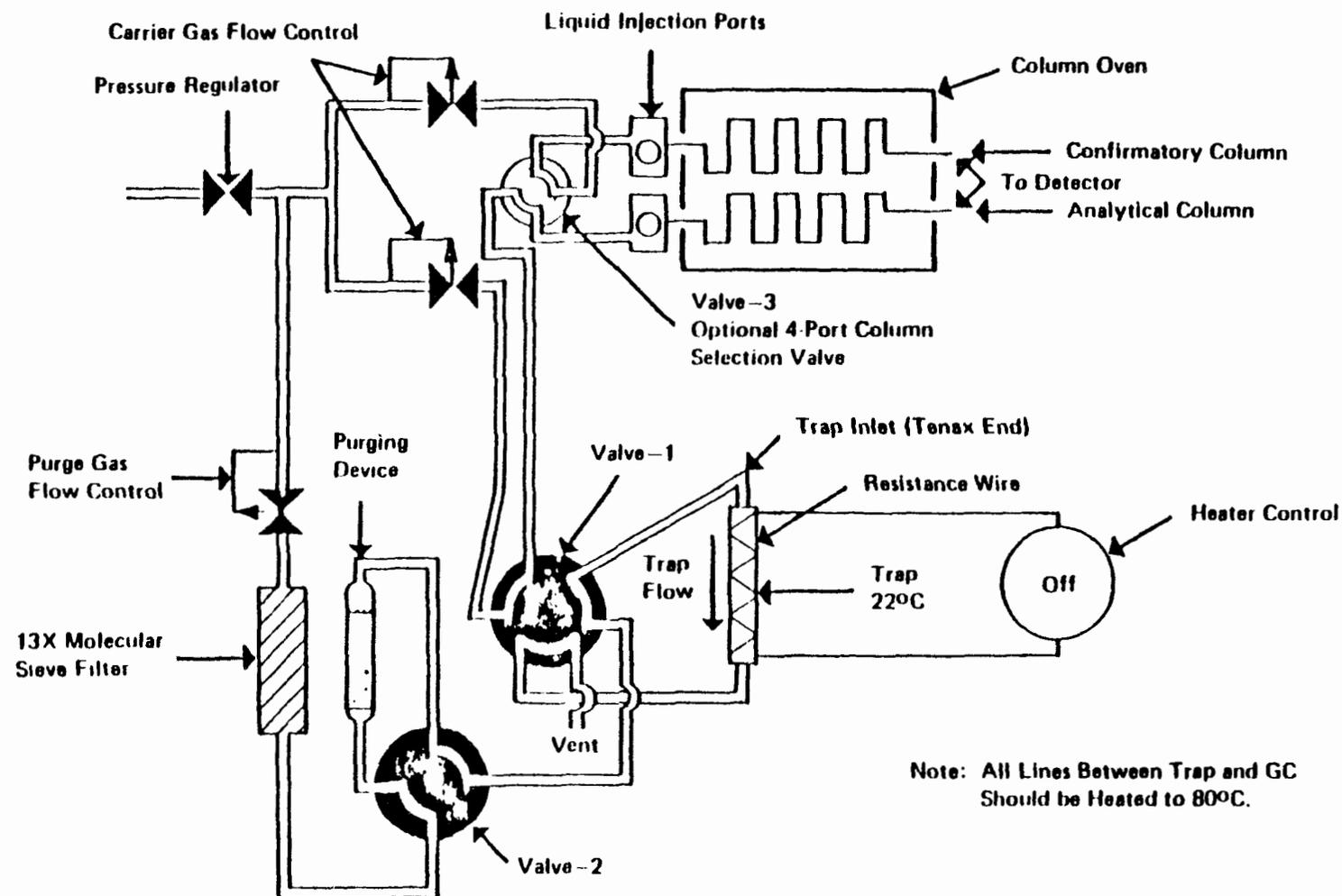


Figure 4. Purge-and-trap system, purge sorb mode, for methods 8010, 8020 and 8030.

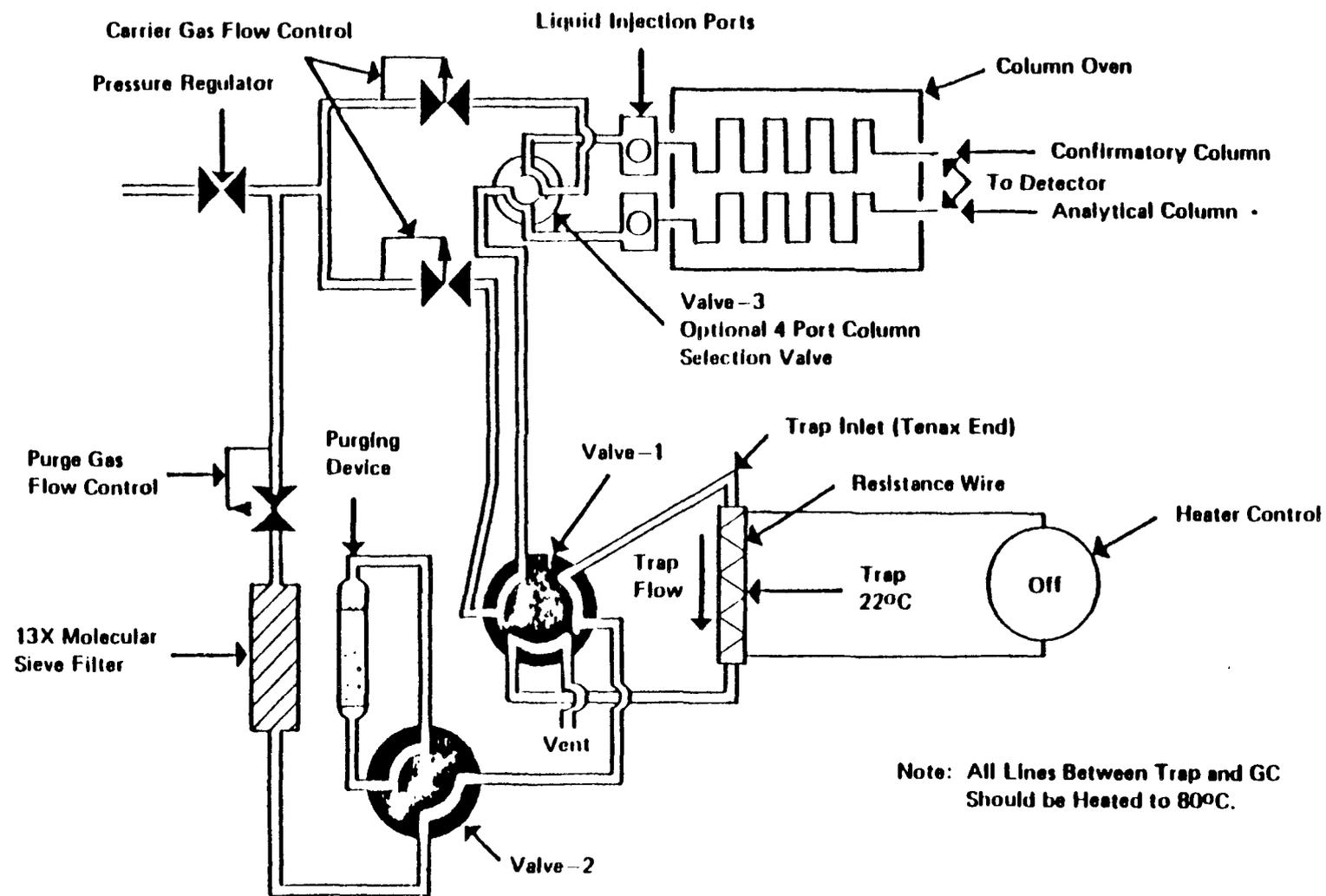


Figure 5. Purge-and trap system, trap dry mode, for Methods 8020 and 8030.

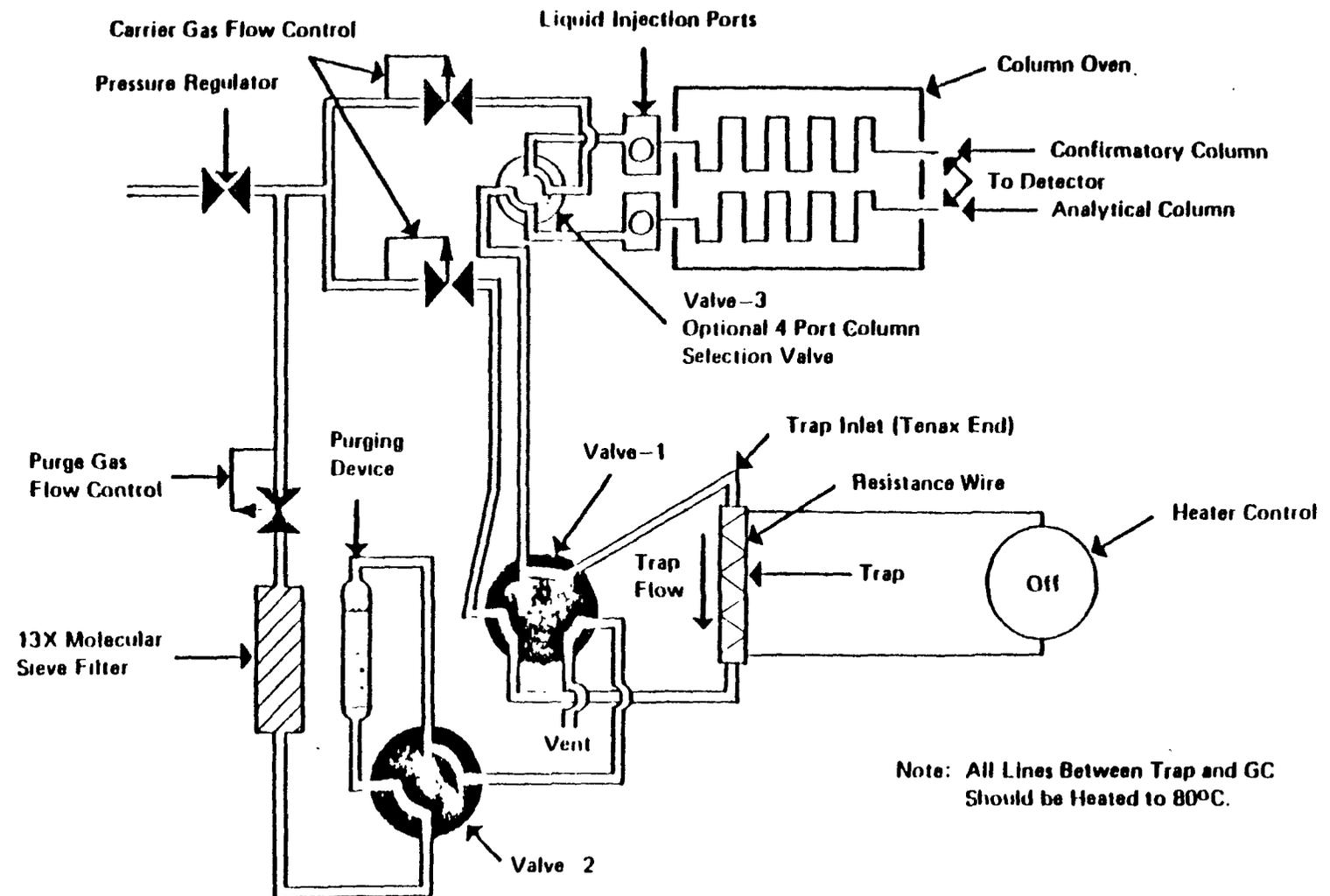


Figure 6. Purge and trap system, desorb mode, for Methods 8010, 8020 and 8030.

5.2 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

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

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

5.3 Reagent PEG (polyethylene glycol; for solid samples): Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferents are not observed at the method detection limit for compounds of interest. Methanol which has been distilled in glass can be used as a substitute for PEG.

5.3.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.3.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Refer to Method 8010, 8020, or 8030 for pertinent information.

## 7.0 Procedures

7.1 Assemble the purge-and-trap device (see Figures 4 through 6). Purge parameters to be used depend on the compounds being analyzed for; see Table 1. Pack the trap as shown in Figure 2 or 3 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 trap for 10 min by backflushing at 180° C.

7.2 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.

7.3 Adjust the purge gas (nitrogen or helium) flow rate according to Table 1.

7.4 Operate the gas chromatograph using the conditions described in the appropriate method, 8010, 8020, or 8030.

7.5 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.

7.6 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. (NOTE: For pastes it may be necessary to dilute the sample by adding a nonvolatile solvent to the sample. In such cases diluting can be performed in the purging device.)

7.7 PEG extraction procedure for solids (methanol which has been distilled in glass can be used as a substitute for PEG). Sample aliquots for extraction should be transferred as quickly as possible to minimize loss of volatiles from the sample.

7.7.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent PEG. Weigh the capped centrifuge tube and PEG on an analytical balance.

7.7.2 Using an appropriate implement, transfer approximately 2 g of sample to the PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the PEG as quickly as possible. Take care not to touch the sample-transfer implement to the PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.7.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.7.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.7.5 Add an aliquot of the sample extract to 5 ml reagent water.

7.8 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 liquid samples for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.

7.9 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. Close both valves and purge the sample for the time specified in Table 1. If Method 8020 will be used for analysis of the sample, dry the trap by maintaining a flow rate of 40 ml/min dry purge for 4 min.

7.10 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 the backflush temperature indicated in Table 1, while backflushing the trap with an inert carrier gas at 20 to 60 ml/min for 4 min. 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° or 50° C.

7.11 Return the purge trap device to the purge mode.

7.12 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution, and distilled water and drying at 105° C.

7.13 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected by heating the trap to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.14 The analysis of blanks is most important in the purge-and-trap technique since the purging device and the trap can become contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water. Blanks should be sealed, stored at 4° C, and analyzed with each group of samples.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

## 9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
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).
4. Ligon, W.V. and H. Grade. 1981. Poly(ethylene glycol) as a diluent for preparation of standards for volatile organics in water. Anal. Chem. 53:920-921.

## METHOD 7040

### ANTIMONY (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7040 is an atomic absorption procedure approved for determining the concentration of antimony in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7040, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the antimony concentration. Background correction must be employed for all analyses.

2.3 Typical detection limits for this method are 0.2 mg/l; typical sensitivities are 0.2 mg/l.

#### 3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Excess concentrations of copper and nickel (and possibly other elements) as well as acids can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

3.3 High lead concentrations may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, a secondary wavelength should be employed.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

## 2 / INORGANIC ANALYTICAL METHODS

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Antimony hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Antimony standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.7426 g of antimony potassium tartrate (analytical reagent grade) in distilled deionized water and dilute to 1 liter.

5.4 Antimony working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting the flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 217.6-nm line is suggested as the analytical wavelength of choice. However, under the conditions discussed in Section 3.3, a less sensitive secondary wavelength may be useful. Background correction should be employed for all analyses.

7.3 Air/acetylene flames should be fuel lean.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of antimony standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 The final calculated concentration should take into account all dilution and concentration factors.

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

#### 4 / INORGANIC ANALYTICAL METHODS

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7041

### ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

#### 1.0 Scope and Application

1.1 Method 7041 is an atomic absorption procedure approved for determining the concentration of antimony in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7041, samples must be prepared in order to convert organic forms of antimony to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the antimony concentration.

2.3 The typical detection limit for this method is 3  $\mu\text{g/l}$ .

#### 3.0 Interferences

3.1 Temperature and times for the dry and char (ash) cycles must be carefully selected since antimony is volatile in the presence of certain chloride salts (e.g., ammonium chloride).

3.2 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, antimony analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

## 2 / INORGANIC ANALYTICAL METHODS

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.5 High lead concentrations may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, a secondary wavelength should be employed.

### 4.0 Apparatus and Materials

4.1 Griffin beakers of assorted sizes.

4.2 Qualitative filter paper.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Antimony hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000  $\mu$ l as required.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrochloric acid (1:1): Prepared from Type II water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Antimony standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.7426 g of antimony potassium tartrate (analytical reagent grade) in Type II water and dilute to 1 liter.

5.5 Antimony working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc.  $\text{HNO}_3$ . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE. Low recoveries for antimony may result if the sample is allowed to go to dryness.) Cool the beaker and add another 3-ml portion of conc.  $\text{HNO}_3$ . Re-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.

7.1.2 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 a small quantity of redistilled 1:1 HCl (5 ml/100 ml of final solution) and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

#### 4 / INORGANIC ANALYTICAL METHODS

7.1.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. (NOTE: Filtration should be done only if there is concern that insoluble materials will clog the nebulizer since this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute nitric acid.) Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.2 The 217.6-nm line is suggested as the analytical wavelength of choice. However, under the condition discussed in Section 3.5, a secondary wavelength may be useful.

7.3 Background correction shall be employed for all analyses.

7.4 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.5 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.6 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.7 Either (1) run a series of antimony standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts and all samples that suffer from matrix interferences.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7060

### ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

#### 1.0 Scope and Application

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 1 µg/l.

#### 3.0 Interferences

3.1 Elemental arsenic and many of its compounds are volatile and therefore samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results.

## 2 / INORGANIC ANALYTICAL METHODS

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

### 4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Arsenic hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000  $\mu$ l as required.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Arsenic standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve

1.320 g of arsenic trioxide ( $\text{As}_2\text{O}_3$ , analytical reagent grade) or equivalent in 100 ml of Type II water containing 4 g NaOH. Acidify the solution with 20 ml conc.  $\text{HNO}_3$  and dilute to 1 liter.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc.  $\text{HNO}_3$ , 2 ml of 30%  $\text{H}_2\text{O}_2$ , and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30%  $\text{H}_2\text{O}_2$  and sufficient conc.  $\text{HNO}_3$  to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

#### 4 / INORGANIC ANALYTICAL METHODS

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5  $\mu\text{g/g}$  dry weight).

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7061

### ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

#### 1.0 Scope and Application

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and groundwater. Method 7061 is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate solution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

#### 2.0 Summary of Method

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the arsenic in the digestate is reduced to the trivalent form using tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the hollow cathode radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/l.

#### 3.0 Interferences

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample workup can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of  $\text{SO}_3$  are observed.

3.3 Elemental arsenic and many of its compounds are volatile and therefore certain samples may be subject to losses of arsenic during sample preparation.

#### 4.0 Apparatus and Materials

4.1 100-ml beaker.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry/hydride generator or a generator constructed from the following materials (see Figure 1).

4.3.1 Medicine dropper that can be fitted into a size "0" rubber stopper and that is capable of delivering 1.5 ml.

4.3.2 50-ml pear-shaped reaction flask with two 14/20 necks (Scientific Glass JM-5835).

4.3.3 Gas inlet-outlet tube constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground glass joint.

4.3.4 Magnetic stirrer to homogenize the zinc slurry.

4.3.5 10-cm polyethylene drying tube filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter capable of measuring 1 liter/minute.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

4.5 Burner recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip chart recorder.

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

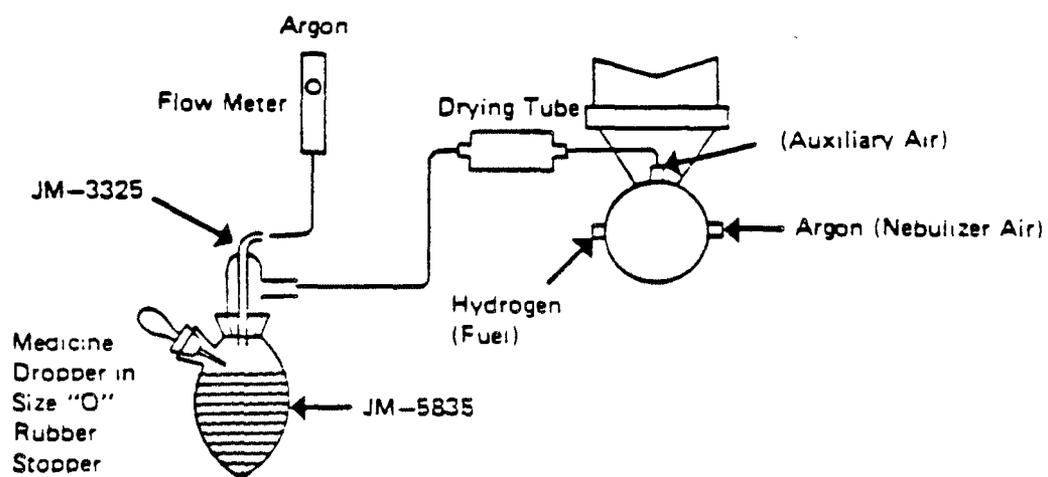


Figure 1. Zinc slurry hydride generator apparatus set-up and AAS sample introduction system.

5.5 Diluent: Add 100 ml 18 N  $H_2SO_4$  and 400 ml concentrated HCl to 400 ml Type II water and dilute to a final volume of 1 liter with Type II water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 ml Type II water.

5.7 Stannous chloride solution: Dissolve 100 g  $SnCl_2$  in 100 ml conc. HCl.

#### 5.8 Arsenic solutions

5.8.1 Arsenic standard solution (1,000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide  $As_2O_3$  (analytical reagent grade) or equivalent in 100 ml of Type II water containing 4 g NaOH. Acidify the solution with 20 ml conc.  $HNO_3$  and dilute to 1 liter.

5.8.2 Intermediate arsenic solution: Pipet 1 ml stock arsenic solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml concentrated  $HNO_3$ /liter (1 ml = 10  $\mu g$  As).

5.8.3 Standard arsenic solution: Pipet 10 ml intermediate arsenic solution into a 100-ml volumetric flask and bring to volume with deionized distilled water containing 1.5 ml concentrated  $HNO_3$ /liter (1 ml = 1  $\mu g$  As).

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and distilled deionized water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Place a 50 ml aliquot of digested sample (or, in the case of analysis of EP extracts, 50 ml) of the material to be analyzed in a 100-ml beaker. Add 10 ml conc.

$\text{HNO}_3$  and 12 ml 18 N  $\text{H}_2\text{SO}_4$ . Evaporate the sample in the hood on an electric hot plate until white  $\text{SO}_3$  fumes are observed (a volume of about 20 ml). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 ml of  $\text{HNO}_3$ . Continue to add additional  $\text{HNO}_3$  in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of  $\text{SO}_3$  fumes, the digestion is complete. Cool the sample, add about 25 ml Type II water, and again evaporate until  $\text{SO}_3$  fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-ml volumetric flask. Add 40 ml of concentrated HCl and bring to volume with Type II water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 ml of standard to 100-ml volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25  $\mu\text{g As/liter}$ .

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 ml from each of these standards into separate 50-ml volumetric flasks. Add 10 ml of the prepared sample to each flask. Bring to volume with Type II water containing 1.5 ml  $\text{HNO}_3/\text{liter}$ .

7.4 Add 10 ml of prepared sample to a 50-ml volumetric flask. Bring to volume with Type II water containing 1.5 ml  $\text{HNO}_3/\text{liter}$ . This is the blank.

NOTE: The absorbance from the blank will be one-fifth that produced by the prepared sample. The absorbance from the spiked standards will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these in mind, the correct dilutions to produce optimum absorbance can be judged.

7.5 Transfer a 25-ml portion of the digested sample or standard to the reaction vessel, and add 1 ml potassium iodide solution. Add 0.5 ml  $\text{SnCl}_2$  solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 ml zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed. CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon hydrogen flame. The argon-hydrogen flame is colorless, so it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-tenth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required then the concentration can be part of the calibration curve.

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7080

### BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7080 is an atomic absorption procedure approved for determining the concentration of barium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7080, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, an ionization suppressant is added and a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the barium concentration. When possible, background correction should be employed.

2.3 The typical detection limit for this method is 0.1 mg/l; typical sensitivity is 0.4 mg/l.

#### 3.0 Interferences

3.1 High hollow cathode current settings and a narrow spectral band pass must be used since both barium and calcium emit strongly at barium's analytical wavelength.

3.2 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. Therefore an ionization suppressant must be added to both standards and samples.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.4 If an air/acetylene flame is used, then the presence of phosphate silicon and aluminum will decrease the sensitivity. This problem can be overcome by adding a releasing agent (e.g., lanthanum) to both samples and standard.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Barium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

#### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Barium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.787 g barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (analytical reagent grade) in Type II water and dilute to 1 liter.

5.4 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

5.5 Lanthanum chloride solution if needed: Dissolve 25 g reagent grade  $\text{La}_2\text{O}_3$  slowly in 250 ml concentrated HCl. (Reaction can be violent.) Dilute to 500 ml with Type II water.

5.6 Barium working standards: Prepare dilutions of the stock barium solution to be used as calibration standards. To each 100 ml of standard and sample add 2.0 ml potassium chloride solution.

5.7 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.8 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 553.6-nm wavelength line shall be used.

7.3 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of barium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 The final calculated concentration should take into account all dilution and concentration factors.

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7081

### BARIUM (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7081 is an atomic absorption procedure approved for determining the concentration of barium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7081, samples must be prepared in order to convert organic forms of barium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the barium concentration.

2.3 The typical detection limit for this method is 2 µg/l.

#### 3.0 Inferences

3.1 Barium is known to form a barium carbide in the graphite furnace. This less volatile carbide can cause losses of sensitivity and memory effects.

3.2 The long residence time and the high concentration of the analyte in the optical path of the graphite furnace can lead to severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

3.4 Halide acids should not be used.

## 2 / INORGANIC ANALYTICAL METHODS

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder.

4.2 Barium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.5 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000  $\mu$ l as required.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Barium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.787 g barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , analytical reagent grade) in Type II water and dilute to 1 liter.

5.4 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

5.5 Barium working standards: Prepare dilution of the stock barium solution to be used as calibration standards. To each 100 ml of standard and sample add 2.0 ml potassium chloride solution.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 553.6-nm line is the analytical wavelength to be used for barium analysis.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of barium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

#### 4 / INORGANIC ANALYTICAL METHODS

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

#### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7130

### CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7130 is an atomic absorption procedure approved for determining the concentration of cadmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7130, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the cadmium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.005 mg/l; typical sensitivity is 0.025 mg/l.

#### 3.0 Interferences

3.1 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Cadmium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

## 2 / INORGANIC ANALYTICAL METHODS

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Cadmium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.282 g cadmium sulfate ( $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ , analytical reagent grade) and dissolve in Type II water or equivalent.

5.4 Cadmium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 228.8-nm wavelength line and background correction shall be employed.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of cadmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

#### 4 / INORGANIC ANALYTICAL METHODS

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7131

### CADMIUM (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7131 is an atomic absorption procedure approved for determining the concentration of cadmium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7131, samples must be prepared in order to convert organic forms of cadmium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the cadmium concentration.

2.3 The typical detection limit for this method is 0.1 µg/l.

#### 3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

## 2 / INORGANIC ANALYTICAL METHODS

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Cadmium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate,  $(\text{NH}_4)_2\text{HPO}_4$  (analytical reagent grade), in Type II water and dilute to 100 ml.

5.4 Cadmium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.282 g of cadmium sulfate ( $3 \text{ CdSO}_4 \cdot 8\text{H}_2\text{O}$ ), analytical reagent grade, in Type II water and dilute to 1 liter.

5.5 Cadmium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 228.8-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 For certain sample types the addition of 2 ml of an ammonium phosphate solution to 100 ml of standards and samples will elevate charring (ashing) temperatures which may eliminate matrix interferences. Ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , has been reported to have a similar effect on these samples.

7.7 Either (1) run a series of cadmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

#### 4 / INORGANIC ANALYTICAL METHODS

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

#### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7190

### CHROMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7190 is an atomic absorption procedure approved for determining the concentration of chromium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7190, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the chromium concentration.

2.3 The typical detection limit for this method is 0.05 mg/l; typical sensitivity is 0.25 mg/l.

#### 3.0 Interferences

3.1 The nitrous oxide/acetylene flame is the recommended flame since chromium analysis in an air/acetylene flame suffers from matrix interferences caused by nickel iron and other metals. If an air/acetylene flame must be used it should be lean.

3.2 An ionization interference may occur in the nitrous oxide flame if the samples have a significantly higher amount of alkali salts than the standards. If this interference is encountered, an ionization suppressant should be added to both samples and standards.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

## 2 / INORGANIC ANALYTICAL METHODS

4.2 Chromium hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Chromium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.923 g of chromium trioxide ( $\text{CrO}_3$ , reagent grade) in Type II water, acidify with redistilled  $\text{HNO}_3$  and dilute to 1 liter.

5.4 Chromium working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Nitrous oxide cylinder.

5.6 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.7 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 357.9-nm wavelength line and background correction shall be employed.

7.3 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

#### 4 / INORGANIC ANALYTICAL METHODS

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7191

### CHROMIUM (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7191 is an atomic absorption procedure approved for determining the concentration of chromium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7191, samples must be prepared in order to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the chromium concentration.

2.3 The typical detection limit for this method is 1 µg/l.

#### 3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Low concentrations of calcium may cause interferences; at concentrations above 200 mg/l, calcium's effect is constant. Calcium nitrate (see Section 5.4) is therefore added to ensure a known constant effect.

## 2 / INORGANIC ANALYTICAL METHODS

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Chromium hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%).

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (analytical reagent grade), in Type II water and dilute to 1 liter.

5.5 Chromium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.923 g of chromium trioxide ( $\text{CrO}_3$ , analytical reagent grade) in Type II water and dilute to 1 liter.

5.6 Chromium working standards: These standards should be prepared to contain 0.5% (v/v)  $\text{HNO}_3$ ; 1 ml of 30%  $\text{H}_2\text{O}_2$  and 1 ml of the calcium nitrate solution may be added to lessen interferences.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 357.9-nm wavelength line shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

#### 4 / INORGANIC ANALYTICAL METHODS

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

#### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7195

### HEXAVALENT CHROMIUM: COPRECIPITATION METHOD

#### 1.0 Scope and Application

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium Cr(VI) in Extraction Procedure toxicity characteristic (EP) extracts and groundwaters. This method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present (see paragraph 3.1).

1.2 Method 7195 may be used to analyze samples containing more than 5 µg of Cr(VI) per liter using either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

#### 2.0 Summary of Method

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate (containing Cr(III)) is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid, and quantified as chromium Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

#### 3.0 Interferences

3.1 Extracts containing either sulfate or chloride in concentrations above 1000 mg/l should be diluted prior to analysis.

#### 4.0 Apparatus and Materials

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-ml capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

## 2 / INORGANIC ANALYTICAL METHODS

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  (analytical reagent grade), in Type II water and dilute to 100 ml.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$  (analytical reagent grade), in Type II water and dilute to 100 ml.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (analytical reagent grade), in Type II water and dilute to 100 ml (1 ml = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 ml glacial acetic acid,  $\text{CH}_3\text{COOH}$  (ACS reagent grade), to 100 ml with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 ml concentrated ammonium hydroxide,  $\text{NH}_4\text{OH}$  (analytical reagent grade), to 100 ml with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate,  $\text{K}_2\text{Cr}_2\text{O}_7$  (analytical reagent grade), in Type II water and dilute to 1 liter (1 ml = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 ml of the potassium dichromate standard solution, add 1 ml of 30%  $\text{H}_2\text{O}_2$  and 1 ml concentrated  $\text{HNO}_3$  and dilute to 100 ml with Type II water (1 ml = 5.0 mg trivalent chromium). Prepare fresh monthly or as needed.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4° C until analyzed.

## 7.0 Procedure

7.1 Transfer a 50-ml portion of the sample to a 100-ml Griffin beaker and adjust to a pH of  $3.5 \pm 0.3$  by adding volumes of 10% acetic acid dropwise. Proceed immediately to 7.2 taking no longer than 15 min between these steps. NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to less than 3, 10%  $\text{NH}_4\text{OH}$  should be used to readjust the pH to  $3.5 \pm 0.3$ .

7.2 Pipet a 10-ml aliquot of the adjusted sample into a centrifuge tube. Add 100  $\mu\text{l}$  of the lead nitrate solution, stopper the tube, mix the sample and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 ml glacial acetic acid, stopper and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100  $\mu\text{l}$  of ammonium sulfate solution, stopper and mix.

7.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2000 rpm in small increments over a period of 5 min. Hold at 2000 rpm for 1 min. NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care the supernate can be withdrawn to within approximately 0.1 ml above the precipitate. Wash the precipitate with 5 ml Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

7.7 To the remaining precipitate, add 0.5 ml concentrated  $\text{HNO}_3$ , 100  $\mu\text{l}$  30%  $\text{H}_2\text{O}_2$  and 100  $\mu\text{l}$  calcium nitrate solution. Stopper the tube and mix using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 ml, mix and analyze in the same manner as the calibration standard.

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/liter. Add to the blank and each standard, before diluting to final volume, 1 ml 30%  $\text{H}_2\text{O}_2$ , 5 ml concentrated  $\text{HNO}_3$ , and 1 ml calcium nitrate solution for each 100 ml of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

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7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100  $\mu\text{g Cr/liter}$ . Add to the blank and each standard before diluting to final volume, 1 ml 30%  $\text{H}_2\text{O}_2$ , 5 ml concentrated  $\text{HNO}_3$ , and 1 ml calcium nitrate solution for each 100 ml of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

### 7.10 Verification

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-ml aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30  $\mu\text{g Cr(VI)/liter}$ . To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution, and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (chelation/extraction or colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be made by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/liter Cr(VI), one can conclude that the analytical method has been verified and the waste is not hazardous by reason of the Cr(VI) concentration in the EP extract.

7.12 If none of the analytical methods approved for this analysis yield valid results, and if the sample contains more total chromium than the threshold amount of hexavalent chromium, the sample will be considered to exhibit the characteristic of EP toxicity unless exempted according to the provisions of 40 CFR 261.4(b)(6).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7196

### HEXAVALENT CHROMIUM: COLORIMETRIC METHOD

#### 1.0 Scope and Application

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium Cr(VI) in Extraction Procedure toxicity characteristic (EP) extracts and groundwaters. This method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present (See paragraph 3.1).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

#### 2.0 Summary of Method

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product and its absorbance is measured photometrically at 540 nm.

#### 3.0 Interferences

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/l of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/liter may produce a yellow color but the ferric iron color is not strong and no difficulty is normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

#### 4.0 Apparatus and Materials

4.1 Colorimetric equipment. One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate,  $K_2Cr_2O_7$  (analytical reagent grade), in Type II water and dilute to 1 liter (1 ml = 50  $\mu$ g Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 ml potassium dichromate stock solution to 100 ml (1 ml = 5  $\mu$ g Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 ml of distilled reagent grade or spectrograde quality sulfuric acid,  $H_2SO_4$ , to 100 ml with Type II water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 ml acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4° C until analyzed.

## 7.0 Procedure

7.1 Color development and measurement: Transfer 95 ml of the extract to be tested to a 100-ml volumetric flask. Add 2.0 ml diphenylcarbazide solution and mix. Add  $H_2SO_4$  solution to give a pH of  $2 \pm 0.5$ , dilute to 100 ml with Type II water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use Type II water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of

a blank carried through the method (see also note below). From the corrected absorbance, determine the mg/l of chromium present by reference to the calibration curve. NOTE: If the solution is turbid after dilution to 100 ml in 7.1 above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

## 7.2 Preparation of calibration curve

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-ml beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/l Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell, and measure the absorbance at 540 nm. As reference, use distilled water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/l of Cr(VI).

## 7.3 Verification

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-ml aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30  $\mu\text{g}$  Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution, and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (coprecipitation or chelation/extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be made by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/l Cr(VI), one can conclude that the analytical method has been verified and the waste is not hazardous by reason of the Cr(VI) concentration in the EP extract.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 If none of the analytical methods approved for this analysis yield valid results, and if the sample contains total chromium in excess of the threshold concentration allowed for hexavalent chromium, the sample will be considered to exhibit the characteristic of EP toxicity unless exempted according to the provisions of 40 CFR 261.4(b)(6).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Analyze check standards after approximately every 15 samples.

8.5 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.6 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.7 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7197

### HEXAVALENT CHROMIUM: CHELATION/EXTRACTION

#### 1.0 Scope and Application

1.1 Method 7197 is approved for determining the concentration of dissolved hexavalent chromium Cr(VI) in Extraction Procedure toxicity characteristic (EP) extracts and groundwaters. This method may also be applicable to certain domestic and industrial wastes provided that no interfering substances are present (see paragraph 3.1).

1.2 Method 7197 may be used to analyze samples containing from 1.0 to 25 µg of Cr(VI) per liter.

#### 2.0 Summary of Method

2.1 Method 7197 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer.

#### 3.0 Interferences

3.1 High concentrations of other metals may interfere.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp.

4.3 Strip chart recorder (optional).

#### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in Type II water and dilute to 100 ml. Prepare fresh daily.

5.3 Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 ml 50% ethanol.

5.4 Potassium dichromate standard solution I (1.0 ml = 100 µg Cr): Dissolve 0.2829 g pure, dried potassium dichromate,  $K_2Cr_2O_7$ , in Type II water and dilute to 1000 ml.

5.5 Potassium dichromate standard solution II (1.0 ml = 10.0 µg Cr): Dilute 100 ml chromium standard solution I to 1 liter with Type II water.

5.6 Potassium dichromate standard solution III (1.0 ml = 0.10 µg Cr): Dilute 10.0 ml chromium standard solution II to 1 liter with Type II water.

5.7 Methyl isobutyl ketone (MIBK), analytical reagent grade: Avoid or redistill material that comes in contact with metal or metal-lined caps.

5.8 Sodium hydroxide solution, 1 M: Dissolve 40 g sodium hydroxide, NaOH (ASC reagent grade), in Type II water and dilute to 1 liter.

5.9 Sulfuric acid, 0.12 M: Slowly add 6.5 ml distilled reagent grade or spectrograde quality sulfuric acid,  $H_2SO_4$ , with Type II water and dilute to 1 liter.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the chelation and extraction should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4° C until analyzed.

## 7.0 Procedure

7.1 Pipet a volume of extract containing less than 2.5 µg chromium (100 ml maximum) into a 200-ml volumetric flask, and adjust the volume to approximately 100 ml.

7.2 Prepare a blank and sufficient standards, and adjust the volume of each to approximately 100 ml.

7.3 Add 2 drops of bromphenol blue indicator solution. (The pH adjustment to 2.4 may also be made with a pH meter instead of using an indicator.)

## METHOD 7420

### LEAD (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7420 is an atomic absorption procedure approved for determining the concentration of lead in wastes, mobility procedure extracts, and soils. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7420, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the lead concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.1 mg/l; typical sensitivity is 0.5 mg/l.

#### 3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Lead hollow cathode lamp or electrodeless discharge lamp.

4.3 Strip chart recorder (optional).

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### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.599 g of lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  (analytical reagent grade), and dissolve in Type II water, acidify with 10 ml redistilled  $\text{HNO}_3$ , and dilute to 1 liter with Type II water.

5.4 Lead working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H<sub>2</sub>SO<sub>4</sub> dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 ml of 0.12 M H<sub>2</sub>SO<sub>4</sub> in excess. The pH at this point should be 2.4.

7.5 Add 5.0 ml APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 ml MIBK and shake vigorously for 3 min.

7.7 Allow the layers to separate and add Type II water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.9 Determine the mg/liter of Cr(VI) in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples.

#### 7.10 Verification

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting chelation. This must be accomplished by analyzing a second 10-ml aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 µg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution, and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.10.4 If the interference persists after sample dilution, an alternative method (coprecipitation or colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be made by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less

than 5 mg/l Cr(VI), one can conclude that the analytical method has been verified and the waste is not hazardous by reason of the Cr(VI) concentration in the EP extract.

7.12 If none of the analytical methods approved for this analysis yield valid results, and if total chromium concentrations are in excess of the threshold limits allowed for hexavalent chromium, the sample will be considered to exhibit the characteristic of EP toxicity unless exempted according to the provisions of 40 CFR 261.4(b)(6).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 283.3-nm wavelength line and background correction shall be used.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of lead standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

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8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7421

### LEAD (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7421 is an atomic absorption procedure approved for determining the concentration of lead in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7421, samples must be prepared in order to convert organic forms of lead to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the lead concentration.

2.3 The typical detection limit for this method is 1 µg/l.

#### 3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe *physical and chemical interferences*. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, lead analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. *Simultaneous background correction must be employed to avoid erroneously high results.*

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

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3.4 Sulfate can suppress lead absorbance. This interference can be eliminated or lessened by adding a lanthanum releasing agent (10 ml lanthanum solution per 100 ml of solution).

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Lead hollow cathode lamp or electrodeless discharge lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lanthanum nitrate solution: Dissolve 58.64 g of ACS reagent grade  $\text{La}_2\text{O}_3$  in 100 ml concentrated  $\text{HNO}_3$  and dilute to 1000 ml with Type II water.

5.4 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 1.599 g lead nitrate,  $\text{Pb}(\text{NO}_3)_2$  (analytical reagent grade), in Type II water and acidify with 10 ml redistilled  $\text{HNO}_3$ . Dilute to 1 liter.

5.5 Lead working standards: These standards should be prepared such that they contain 0.5% (v/v)  $\text{HNO}_3$ .

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedures

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 283.3-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of lead standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

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7.8 If sulfate interference is encountered, add 10 ml of lanthanum solution to each 100 ml of solution.

7.9 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.10 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.11 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

#### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7470

### MERCURY (MANUAL COLD-VAPOR TECHNIQUE)

#### 1.0 Scope and Application

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility procedure extracts, aqueous wastes and groundwaters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis, the samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

#### 3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

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3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

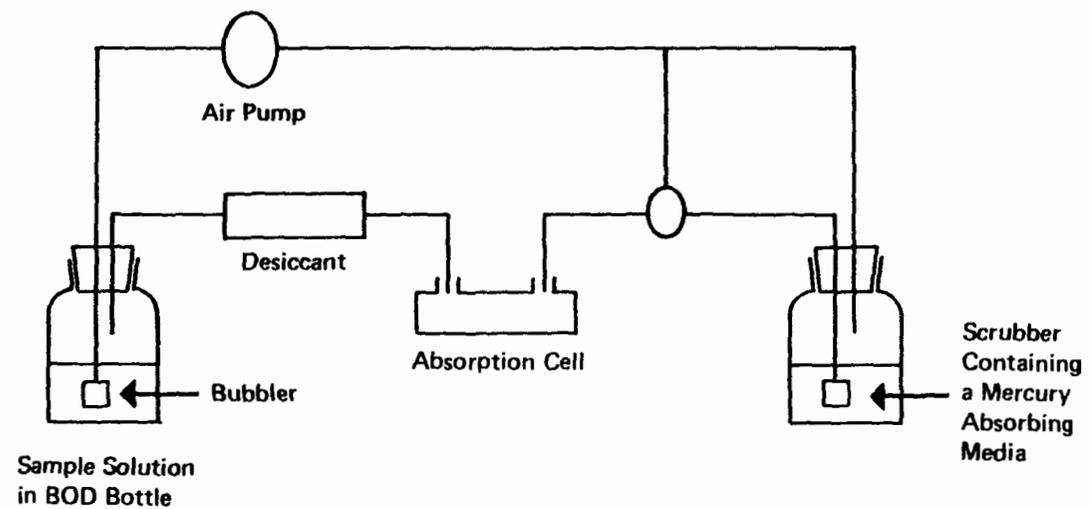


Figure 1. Apparatus for flameless mercury determination.

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4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$
2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Jarnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

#### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sulfuric acid, conc.: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

5.4 Nitric acid, conc.: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 ml of Type II water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of Type II water. Add 10 ml of conc.  $\text{HNO}_3$  and adjust the volume to 100.0 ml (2 ml = 1 mg Hg).

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per ml. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before addition of the aliquot.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid. The suggested maximum holding times for these samples are 38 days in glass containers and 13 in plastic containers.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 µg of mercury, to a 300-ml BOD bottle. Add 5 ml of sulfuric acid and 2.5 ml of conc. nitric acid, mixing after each addition. Add 15 ml of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-ml aliquots of the mercury working standard containing 0 to 1.0 µg of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid and 2.5 ml of conc. nitric acid to each bottle. Add 15 ml of  $\text{KMnO}_4$  solution to each bottle and allow to stand at least 15 min. Add 8 ml of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 ml of the stannous sulfate solution, and immediately attach the bottle to the aeration apparatus and continue as described in Section 7.3.

## 6 / INORGANIC ANALYTICAL METHODS

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration.

7.4 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.7 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7471

### MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

#### 1.0 Scope and Application

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis the samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/l.

#### 3.0 Interferences

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/l of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/l had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) since, during the oxidation step, chlorides are converted to free chlorine which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 ml). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit having a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10° C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.10 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

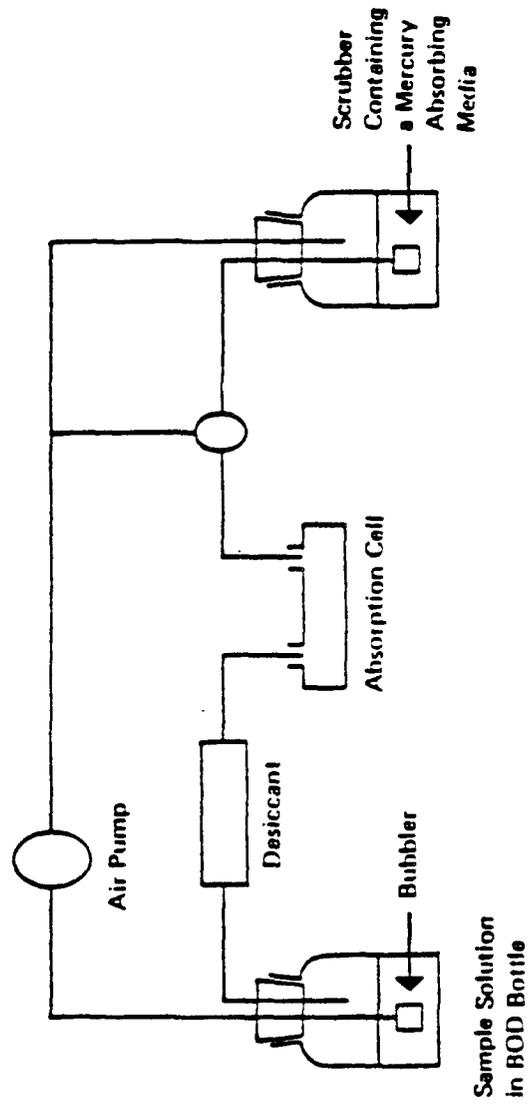


Figure 1. Apparatus for flameless mercury determination.

4.11 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as:

1. equal volumes of 0.1 M  $\text{KMnO}_4$  and 10%  $\text{H}_2\text{SO}_4$
2. 0.25% iodine in a 3% KI solution

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and N. Cassidy St., Columbus, Ohio 43219, Cat. #580-13 or #580-22.

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc.  $\text{HNO}_3$ .

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in Type II water and dilute to 100 ml. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 ml of Type II water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 ml of distilled water. Add 10 ml of conc. nitric acid and adjust the volume to 100.0 ml (1.0 ml = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1  $\mu\text{g}/\text{ml}$ . This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before adding the aliquot.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 For solids or semi-solids, moisture may be driven off in a drying oven at a temperature of 60° C.

## 7.0 Procedure

7.1 Sample preparation: Weigh triplicate 0.2-g portions of dry sample and place in the bottom of a BOD bottle. Add 5 ml of Type II water and 5 ml of aqua regia. Heat 2 min in a water bath at 95° C. Cool, add 50 ml Type II water and 15 ml potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95° C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Add 55 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 ml of conc.  $H_2SO_4$  and 2 ml of conc.  $HNO_3$  are added to the 0.2 g of sample. Add 5 ml of saturated  $KMnO_4$  solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121° C and 15 lb for 15 min. Cool, dilute to a volume of 100 ml with Type II water and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-ml aliquots of the mercury working standard containing 0 to 1.0  $\mu g$  of mercury to a series of 300-ml BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia and heat 2 min in a water bath at 95° C. Allow the sample to cool and add 50 ml Type II water and 15 ml of  $KMnO_4$  solution to each bottle and return to the water bath for 30 min. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 ml of Type II water. Treating each bottle individually, add 5 ml of stannous sulfate solution and immediately attach to bottle to the aeration apparatus and continue as described in Section 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen

levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbance of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7520

### NICKEL (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7520 is an atomic absorption procedure approved for determining the concentration of nickel in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7520, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3010). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the nickel concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.04 mg/l; typical sensitivity is 0.15 mg/l.

#### 3.0 Interferences

3.1 Background correction is required since nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 High concentrations of iron, cobalt and chromium can suppress nickel absorbance. If this interference becomes measurable, either the method of matrix matching or a nitrous oxide/acetylene flame should be employed.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Nickel hollow cathode lamp.

4.3 Strip chart recorder (optional).

## 2 / INORGANIC ANALYTICAL METHODS

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Nickel standard stock solution (1000 mg/l). Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 4.953 g of nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (analytical reagent grade), in Type II water. Add 10 ml of conc. nitric acid and dilute to 1 liter with Type II water.

5.4 Nickel working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions, by replacing the cylinder before the pressure has fallen to 50 psig.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

### 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3010; sludge-type samples should be prepared according to Method

3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 232.0-nm wavelength line and background correction shall be employed.

7.3 An oxidizing air/acetylene flame shall be used.

7.4 Follow the manufacturer's operating instructions for all other instrument parameters.

7.5 Either (1) run a series of nickel standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

#### 4 / INORGANIC ANALYTICAL METHODS

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7521

### NICKEL (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7521 is an atomic absorption procedure approved for determining the concentration of nickel in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7521, samples must be prepared in order to convert organic forms of nickel to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to an acid digestion procedure (Method 3020). Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the nickel concentration.

2.3 The typical detection limit for this method is 1 µg/l.

#### 3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, nickel analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

## 2 / INORGANIC ANALYTICAL METHODS

### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Nickel hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Nickel standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 4.953 g of nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (analytical reagent grade), in Type II water.

5.4 Nickel working standards: These standards should be prepared with the same type and same concentration of acid that will be found in the analytical solution.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Method 3020; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 The 232.0-nm wavelength line and background correction shall be used.

7.3 Follow the manufacturer's operating instructions for all other spectrometer parameters.

7.4 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.5 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.6 Either (1) run a series of nickel standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.6 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

## 4 / INORGANIC ANALYTICAL METHODS

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7740

### SELENIUM (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 µg/l.

#### 3.0 Interferences

3.1 Elemental selenium and many of its compounds are volatile and therefore samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestate prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction must be employed to avoid erroneously high results.

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3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (more than 800 mg/l) and sulfate (more than 200 mg/l). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

### 4.0 Apparatus and Materials

4.1 250-ml Griffin beaker.

4.2 10-ml volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.4 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1000  $\mu$ l as required.

### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Selenium standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6%  $\text{H}_2\text{SeO}_3$ , analytical reagent grade) or equivalent in Type II water and dilute to 200 ml.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or equivalent in Type II water and dilute to 100 ml.

5.6 Nickel nitrate solution (1%): Dilute 20 ml of the 5% nickel nitrate to 100 ml with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. Withdraw appropriate aliquots of the stock solution, add 1 ml of conc.  $\text{HNO}_3$ , 2 ml of 30%  $\text{H}_2\text{O}_2$ , and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Sections 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050, and samples containing oils, greases, or waxes may be prepared according to Methods 3030 or 3040. The applicability

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of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 ml of well-mixed sample to a 250-ml Griffin beaker, add 2 ml of 30%  $\text{H}_2\text{O}_2$  and sufficient conc.  $\text{HNO}_3$  to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95° C or until the volume is slightly less than 50 ml.

7.1.2 Cool and bring back to 50 ml with Type II water.

7.1.3 Pipet 5 ml of this digested solution into a 10-ml volumetric flask, add 1 ml of the 1% nickel nitrate solution and dilute to 10 ml with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other instrument parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured  $\mu\text{l}$  aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.8 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors

must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7741

### SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

#### 1.0 Scope and Application

1.1 Method 7741 is an atomic absorption procedure which is approved for determining the concentration of selenium in wastes, mobility procedure extracts, soils, and groundwater, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste.

#### 2.0 Summary of Method

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to the +4 form using tin chloride. The +4 selenium is then converted to a volatile hydride with hydrogen produced from a zinc/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer, and the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/l.

#### 3.0 Interferences

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample workup can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of  $\text{SO}_3$  are observed.

3.3 Elemental selenium and many of its compounds are volatile and therefore certain samples may be subject to losses of selenium during sample preparation.

#### 4.0 Apparatus and Materials

4.1 100-ml beaker.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1).

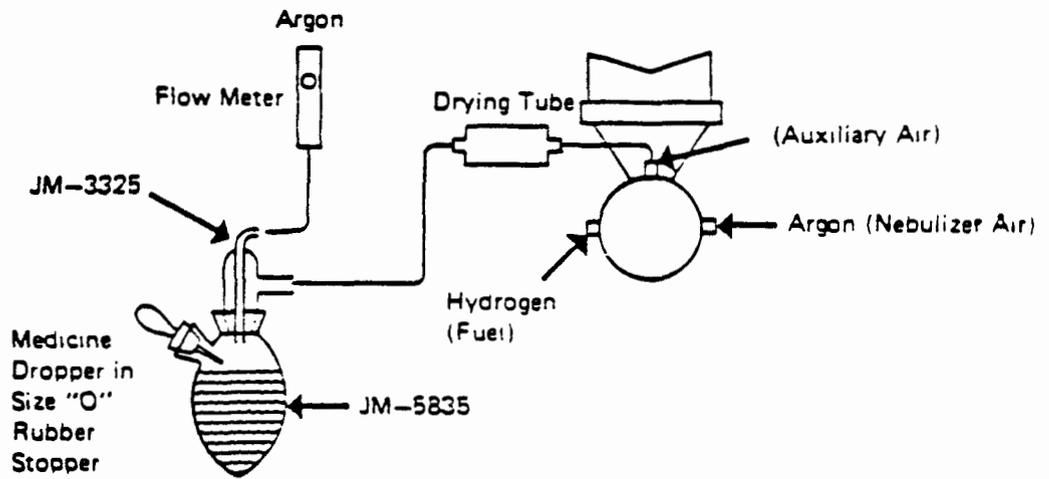


Figure 1. Zinc slurry hydride generator apparatus set-up and AAS sample introduction system.

4.3.1 Medicine dropper fitted into a size "0" rubber stopper capable of delivering 1.5 ml.

4.3.2 A 50-ml pear-shaped reaction flask with two 14/20 necks (Scientific Glass JM-5835).

4.3.3 Gas inlet-outlet tube constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer to homogenize the zinc slurry.

4.3.5 A 10-cm polyethylene drying tube filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip chart recorder and simultaneous background correction.

4.5 Burner recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip chart recorder.

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected all analyses should be blank-corrected.

5.5 Diluent: Add 100 ml 18 N  $H_2SO_4$  and 400 ml concentrated HCl to 400 ml Type II water and dilute to a final volume of 1 liter with Type II water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 ml Type II water.

5.7 Stannous chloride solution: Dissolve 100 g  $\text{SnCl}_2$  in 100 ml of conc. HCl.

5.8 Selenium standard stock solution: 1000 mg/liter solution may be purchased, or prepared as follows. Dissolve 0.3453 g of selenious acid (assay 94.6% of  $\text{H}_2\text{SeO}_3$ ) in Type II water. Add to a 200-ml volumetric flask and bring to volume (1 ml = 1 mg Se).

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated where possible, and analyzed as soon as possible.

## 7.0 Procedure

### 7.1 Sample preparation

7.1.1 To a 50 ml aliquot of digested sample (or in the case of EP extracts a 50-ml sample) add 10 ml conc.  $\text{HNO}_3$  and 12 ml of 18 N  $\text{H}_2\text{SO}_4$ . Evaporate the sample on a hot plate until white  $\text{SO}_3$  fumes are observed (a volume of about 20 ml). Do not let it char. If it chars, stop the digestion, cool and add additional  $\text{HNO}_3$ . Maintain an excess of  $\text{HNO}_3$  (evidence of brown fumes) and do not let the solution darken, because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of  $\text{SO}_3$  fumes, the digestion is complete.

7.1.2 Cool the sample, add about 25 ml distilled deionized water and again evaporate to  $\text{SO}_3$  fumes just to expel oxides of nitrogen. Cool. Add 40 ml conc. HCl and bring to a volume of 100 ml with distilled deionized water.

7.2 Prepare working standards from the standard stock solutions. The following procedure provides standards in the optimum working range.

7.2.1 Pipet 1 ml stock solution into a 1-liter volumetric flask. Bring to volume with Type II water containing 1.5 ml conc.  $\text{HNO}_3$ /liter. The concentration of this solution is 1 mg Se/liter (1 ml = 1  $\mu\text{g}$  Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the selenium stock standard (see Section 5.8) into a 100-ml volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20 and 25  $\mu\text{g}$  Se/liter.

### 7.3 Standard additions

7.3.1 Take the 15-, 20-, and 25- $\mu\text{g}$  standards and transfer quantitatively 25 ml from each into separate 50-ml volumetric flasks. Add 10 ml of the prepared sample to each. Bring to volume with Type II water containing 1.5 ml  $\text{HNO}_3$ /liter.

7.3.2 Add 10 ml of prepared sample to a 50-ml volumetric flask. Bring to volume with Type II water containing 1.5 ml  $\text{HNO}_3$  per liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless so it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-ml portion of the digested sample or standard to the reaction vessel. Add 0.5 ml  $\text{SnCl}_2$  solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 ml zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

7.7 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. For example, if the method of standard additions was employed, the analytical value will be one-tenth the concentration of the original sample due to dilution during preparation. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7760

### SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)

#### 1.0 Scope and Application

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/l; typical sensitivity is 0.06 mg/l.

#### 3.0 Interferences

3.1 Background correction should be employed since nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble so hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

- 4.2 Silver hollow cathode lamp.
- 4.3 Strip chart recorder (optional).

## 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.4 Silver standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate ( $\text{AgNO}_3$ ), analytical reagent grade, in Type II water. Add 5 ml conc.  $\text{HNO}_3$  and bring to volume in a 500-ml volumetric flask (1 ml = 1 mg Ag).

5.5 Silver working standards: These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.6 Iodine solution, IN: Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 ml Type II water. Add 12.7 g iodine ( $\text{I}_2$ ), analytical reagent grade, and dilute to 100 ml. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 ml deionized distilled water add 4.0 ml conc.  $\text{NH}_4\text{OH}$ , 6.5 g KCN, and 5.0 ml of iodine solution. Mix and dilute to 100 ml with deionized distilled water. Do not keep longer than 2 weeks. CAUTION: This reagent cannot be mixed with any acid solutions since toxic hydrogen cyanide will be produced.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 When possible standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Sections 7.2 and 7.3; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

### 7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc.  $\text{HNO}_3$ . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc.  $\text{HNO}_3$ . Re-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. Note, if the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic type samples.

7.2.2 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 a small quantity of  $\text{HNO}_3$  so that the final dilution contains 0.5% (v/v)  $\text{HNO}_3$ , and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the

volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. CAUTION: This can only be done after digestion to prevent formation of toxic hydrogen cyanide under acid conditions. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. CAUTION: cyanogen iodide must not be added to the acidified silver standards. New standards must be made as directed in Sections 5.4 and 5.5 except that the acid addition step must be omitted. Transfer 10 ml of stock solution to a small beaker. Add Type II water to make about 80 ml. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 ml cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100 ml volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be employed.

7.5 An oxidizing air/acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.7 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.9 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

## METHOD 7761

### SILVER (ATOMIC ABSORPTION, FURNACE METHOD)

#### 1.0 Scope and Application

1.1 Method 7761 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and groundwater. All samples must be subjected to an appropriate dissolution step prior to analysis.

#### 2.0 Summary of Method

2.1 Prior to analysis by Method 7761, samples must be prepared in order to convert organic forms of silver to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedures described in Methods 3030 and 3040 may be applicable.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode radiation during atomization will be proportional to the silver concentration.

2.3 The typical detection limit for this method is 0.2  $\mu\text{g/l}$ .

#### 3.0 Interferences

3.1 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, silver analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Silver nitrate solutions are light sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

#### 4.0 Apparatus and Materials

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a strip chart recorder.

4.2 Silver hollow cathode lamp.

4.3 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.4 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

#### 5.0 Reagents

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid: Acid should be analyzed to determine level of impurities. If impurities are detected, all analyses should be blank-corrected.

5.3 Lead standard stock solution (1000 mg/l): Either procure a certified aqueous standard from a supplier (Spex Industries, Alpha Products or Fisher Scientific) and verify by comparison with a second standard, or dissolve 0.7874 g anhydrous silver nitrate ( $\text{AgNO}_3$ ), analytical reagent grade, in Type II water. Add 5 ml concentrated  $\text{HNO}_3$  and bring to volume in a 500-ml volumetric flask.

5.4 Silver working standards: These standards should be prepared with nitric acid such that the final acid concentration is 0.5% (v/v)  $\text{HNO}_3$ .

5.5 Concentrated ammonium hydroxide ( $\text{NH}_4\text{OH}$ ): Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.6 Iodine solution (IN): Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 ml Type II water. Add 12.7 g iodine ( $\text{I}_2$ ), analytical reagent grade, and dilute to 100 ml. Place in a brown bottle.

5.7 Cyanogen iodide solution: To 50 ml deionized distilled water add 4.0 ml concentrated  $\text{NH}_4\text{OH}$ , 6.5 g KCN, and 5.0 ml of iodine solution. Mix and dilute to 100 ml with deionized distilled water. Do not keep longer than 2 weeks. CAUTION: This reagent cannot be mixed with any acid solutions since highly toxic hydrogen cyanide will be produced.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH of less than 2 with nitric acid.

6.4 Nonaqueous samples shall be refrigerated when possible, and analyzed as soon as possible.

## 7.0 Procedure

7.1 Sample preparation: Aqueous samples should be prepared according to Section 7.2; sludge-type samples should be prepared according to Method 3050; and samples containing oils, greases or waxes may be prepared according to Methods 3030 or 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

### 7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a Griffin beaker and add 3 ml of conc.  $\text{HNO}_3$ . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3-ml portion of conc.  $\text{HNO}_3$ . Re-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. Note, if the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic type samples.

7.2.1 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 a small quantity of  $\text{HNO}_3$  so that the final dilution contains 0.5% (v/v)  $\text{HNO}_3$ , and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with distilled water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. CAUTION: This can only be done after digestion to prevent formation of toxic hydrogen cyanide under acid conditions. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. CAUTION: cyanogen iodide must not be added to the acidified silver standards. New standards must be made as directed in Sections 5.4 and 5.5 except that the acid addition step must be omitted. Transfer 10 ml of stock solution to a small beaker. Add Type II water to make about 80 ml. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with Type II water. Add 1 ml cyanogen iodide and allow to stand 1 hr. Transfer quantitatively to a 100-ml volumetric flask and bring to volume with Type II water.

7.4 The 328.1-nm wavelength line and background correction shall be used.

7.5 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.6 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.7 Inject a measured  $\mu$ l aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.8 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.9 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.10 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.11 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.12 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 µg/g dry weight).

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.8 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

SECTION EIGHT

ORGANIC ANALYTICAL METHODS

8.1 Gas Chromatographic Methods (8000-8190)

Methods appropriate for organic analysis of samples by gas chromatography are included on the following pages.

## METHOD 8010

### HALOGENATED VOLATILE ORGANICS

#### 1.0 Scope and Application

1.1 Method 8010 is used to determine the concentration of various halogenated volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8010 may be used to detect the following substances:

Benzyl chloride	1,2-Dichlorobenzene
Bis (2-chloroethoxy)methane	1,3-Dichlorobenzene
Bis (2-chloroisopropyl)ether	1,4-Dichlorobenzene
Bromobenzene	Dichlorodifluoromethane
Bromodichloromethane	1,1-Dichloroethane
Bromoform	1,2-Dichloroethane
Bromomethane	1,1-Dichloroethylene (Vinylidene chloride)
Carbon tetrachloride	trans-1,2-Dichloroethylene
Chloroacetaldehyde	Dichloromethane
Chloral	1,2-Dichloropropane
Chlorobenzene	1,3-Dichloropropylene
Chloroethane	1,1,2,2-Tetrachloroethane
Chloroform	1,1,1,2-Tetrachloroethane
1-Chlorohexane	Tetrachloroethylene
2-Chloroethyl vinyl ether	1,1,1-Trichloroethane
Chloromethane	1,1,2-Trichloroethane
Chloromethyl methyl ether	Trichloroethylene
Chlorotoluene	Trichlorofluoromethane
Dibromochloromethane	Trichloropropane
Dibromomethane	Vinyl chloride

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

#### 2.0 Summary of Method

2.1 Method 8010 provides chromatographic conditions for the detection of halogenated volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a halide-specific detector (HSD).

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.

### 3.0 Interferences

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

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

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

### 4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at

105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including HSD or FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC columns:

Column 1: 8-ft x 0.1-in. I.D. stainless steel or glass column packed with 1% SP-1000 on Carbowax B 60/80 mesh.

Column 2: 6-ft x 0.1-in. I.D. stainless steel or glass column packed with n-octane on Porasil-L 100/120 mesh.

4.6 Detector: Electrolytic conductivity (HSD).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100  $\mu$ l.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5 ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

## 5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds

being analyzed, 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.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Add the assayed reference material

5.3.2.1 Liquids: Using a 100- $\mu$ l syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the alcohol without contacting the neck of the flask.

5.3.2.2 Gases: To prepare standards from any of the organic compounds that boil below 30° C, fill a 5-ml valved gas-tight syringe with the reference standard to the 5-ml mark. Lower the needle to 5 mm above the methyl alcohol meniscus. Slowly inject the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methyl alcohol).

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

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.5 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C and for the 2-chloroethyl-vinyl ether. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20  $\mu$ l of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25- $\mu$ l Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr unless preserved, stored, and sealed according to 6.1 and 6.3.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 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. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl<sub>2</sub>) 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 min.

6.4 All samples must be analyzed within 14 days of collection.

## 7.0 Procedures

7.1 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 45° C for 3 min, then program an 8° C/min temperature rise to 220° C and hold for 15 min.

Column 2: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 50° C for 3 min, then program a 6° C/min temperature rise to 170° C and hold for 4 min.

## 7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

### 7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

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

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured

$A_{iS}$  = Response for the internal standard

$C_{iS}$  = Concentration of the internal standard

$C_S$  = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

### 7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Table 1 summarizes the estimated retention times for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.3.3 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

TABLE 1. ESTIMATED RETENTION TIMES FOR SOME HALOGENATED VOLATILE ORGANICS

Compound	Retention time (min)		Estimated detection limit <sup>a</sup> (µg/l)
	Col. 1	Col. 2	
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
Bromoform	19.2	19.2	0.20
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
Chloroethane	3.33	8.68	0.52
Chloroform	10.7	12.1	0.05
1-Chlorohexane			
2-Chloroethyl vinyl ether	18.0		0.13
Chloromethane	1.50	5.28	0.08
Chlorotoluene			
Dibromochloromethane	16.5	16.6	0.09
Dibromomethane			
1,2-Dichlorobenzene	34.9	23.5	0.15
1,3-Dichlorobenzene	34.0	22.4	0.32
1,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane			
1,1-Dichloroethane	9.30	12.6	0.07
1,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
trans-1,2-Dichloroethylene	10.1	9.38	0.10
Dichloromethane	6.5		
1,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
1,1,2,2-Tetrachloroethane	21.6		0.03
1,1,1,2-Tetrachloroethane			
Tetrachloroethylene	21.7	15.0	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
1,1,2-Trichloroethane	16.5	18.1	0.02
Trichloroethylene	15.8	13.1	0.12
Trichlorofluoromethane	7.18		
Trichloropropane			
Vinyl chloride	2.67	5.28	0.18

<sup>a</sup>Using purge-and-trap method (5030). See also Section 8.3.

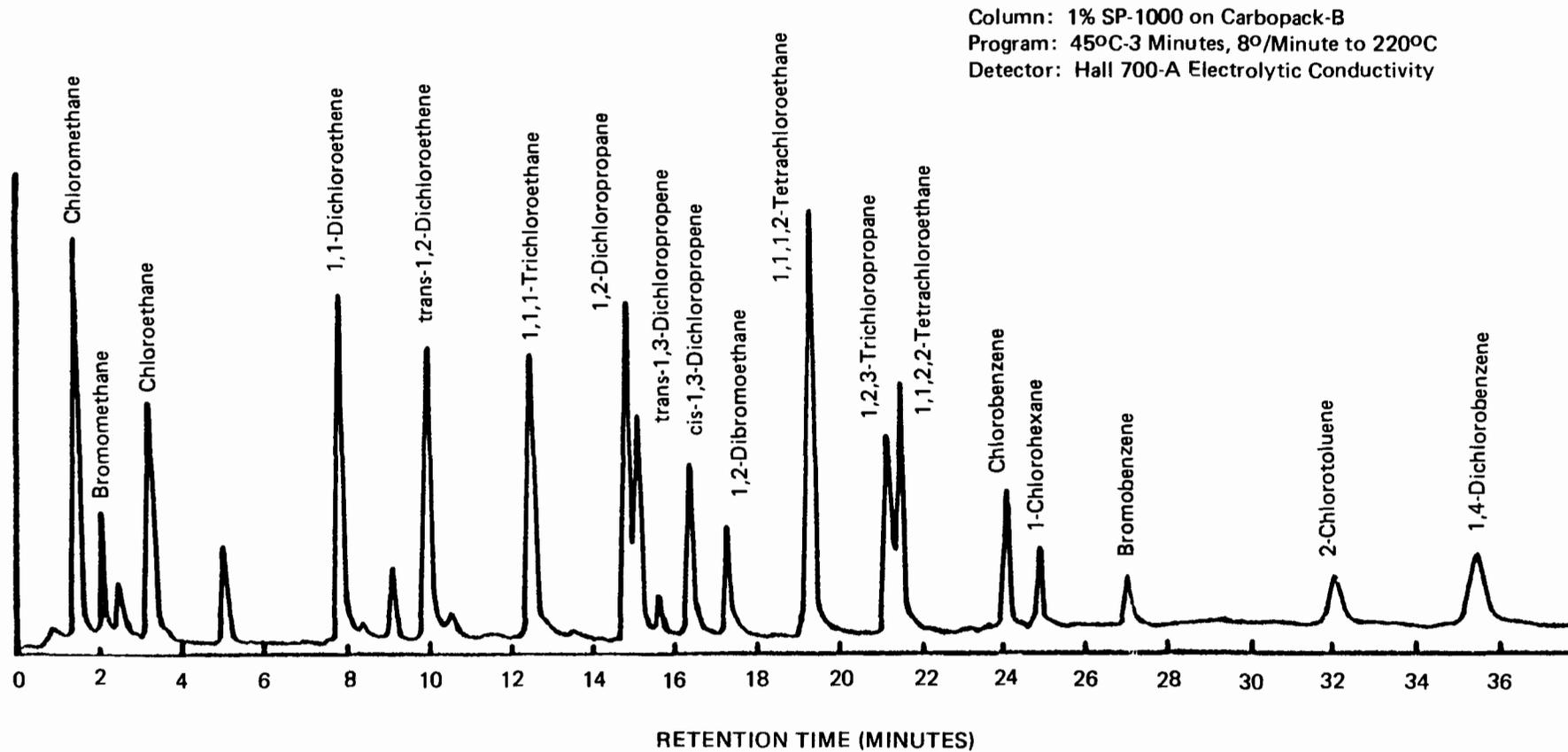


Figure 1. Gas Chromatogram of halogenated volatile organics.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

## 9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
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 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
Bromodichloromethane	100.9	5.0	0.43-46.7	21	3
Bromoform	89.5	9.0	1.45-50	20	3
Carbon tetrachloride	82.5	25.6	0.55-50	19	3
Chlorobenzene	93.9	8.9	2.21-50	20	3
Chloroethane	91.5	22.4	3.95-50	21	3
2-Chloroethylvinyl ether	96.3	9.9	4.39-133	20	3
Chloroform	101.7	20.6	0.44-50	20	3
Chloromethane	91.4	13.4	0.55-23.9	21	3
Dibromochloromethane	98.3	6.5	0.75-93.0	21	3
1,2-Dichlorobenzene	102.0	2.0	4.89-154	21	3
1,3-Dichlorobenzene	91.6	4.3	2.94-46.7	21	3
1,4-Dichlorobenzene	97.5	9.3	2.99-51.6	21	3
1,1-Dichloroethane	102.3	5.5	0.44-46.7	21	3
1,2-Dichloroethane	97.8	4.8	0.44-46.7	21	3
1,1-Dichloroethylene	101.1	21.7	0.37-50	19	3
trans-1,2-Dichloroethylene	91.0	19.3	0.44-98.0	20	3
1,2-Dichloropropane	97.7	8.8	0.29-39.0	21	3
trans-1,3-Dichloropropylene	73.5	17.2	0.43-50	20	3
1,1,2,2-Tetrachloroethane	91.9	15.0	0.46-46.7	21	3
Tetrachloroethylene	94.1	18.1	0.50-35.0	21	3
1,1,1-Trichloroethane	75.1	12.5	0.37-29.0	21	3
1,1,2-Trichloroethane	91.0	25.1	0.45-50	21	3
Trichloroethylene	106.1	7.4	0.38-46.7	21	3
Vinyl chloride	101.9	11.4	0.82-32.3	21	3

## METHOD 8015

### NONHALOGENATED VOLATILE ORGANICS

#### 1.0 Scope and Application

1.1 Method 8015 is used to determine the concentration of nonhalogenated volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8015 is used to detect the following substances:

Acrylamide  
Carbon disulfide  
Diethyl ether  
Methyl ethyl ketone (MEK)  
Methyl isobutyl ketone (MIBK)  
Paraldehyde (trimer of acetaldehyde)

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

#### 2.0 Summary of Method

2.1 Method 8015 provides chromatographic conditions for the detection of certain nonhalogenated volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples can be analyzed by Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

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.

#### 3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should

be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower; they should be less than 1 µg/l.

#### 4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap vial (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

#### 4.5 GC columns:

Column 1: 8-ft x 0.1-in. I.D. stainless steel or glass column packed with 1% SP-1000 on Carbowax B 60/80 mesh.

Column 2: 6-ft x 0.1-in. I.D. stainless steel or glass column packed with n-octane on Porasil-L 100/120 mesh.

4.6 Detector: Flame ionization (FID).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100  $\mu$ l.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5-ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

#### 5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids. Because of the toxicity of many of the compounds being analyzed, 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.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100- $\mu$ l syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the methyl alcohol without contacting the neck of the flask.

5.3.3 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.4 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µl of methanolic standards into 100 ml of reagent water.

5.5.2 Use a 25-µl Hamilton 702N microliter syringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the methanolic standard into the filled volumetric flask below the neck. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded unless stored and sealed as stipulated in Sections 6.1 and 6.3.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 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. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 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  $\text{Cl}_2$ ) 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 min.

6.4 All samples must be analyzed within 14 days of collection.

## 7.0 Procedures

7.1 The recommended gas chromatographic column and operating conditions for the instrument are:

Column 1: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 45° C for 3 min, then program an 8° C/min temperature rise to 220° C and hold for 15 min.

Column 2: Set helium gas flow at 40 ml/min flow rate. Set column temperature at 50° C for 3 min, then program a 6° C/min temperature rise to 170° C and hold for 4 min.

### 7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples.

Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

#### 7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0  $\mu\text{l}$  of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25- $\mu\text{l}$  syringe limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

7.2.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standards is not affected by method or matrix interferences. Because of these limitations, no internal standard that would be applicable to all samples can be suggested.

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured

$A_{iS}$  = Response for the internal standard

$C_{iS}$  = Concentration of the internal standard

$C_S$  = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

### 7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

## 9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
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).

## METHOD 8020

### AROMATIC VOLATILE ORGANICS

#### 1.0 Scope and Application

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8020 may be used to detect the following substances:

- Benzene
- Chlorobenzene
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- Ethyl benzene
- Toluene
- Xylenes (Dimethyl benzenes)

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

#### 2.0 Summary of Method

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

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.

#### 3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample

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syringe or purging device must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high levels of volatile organics, it may be necessary to wash out the syringe or purging device with a detergent solution, rinse it with distilled water, and then dry it in a 105° C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

### 4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap vial (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hour) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including PID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

#### 4.5 GC columns:

Column 1: 6-ft x 0.082-in. I.D. #304 stainless steel or glass tubing. Packed with 5% SP-1200 + 1.75% Bentone 34 on 100/120 mesh Supelcoport.

Column 2: 6-ft x 0.1-in. I.D. #304 stainless steel or glass tubing packed with 5% 1,2,3-tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW.

4.6 Detector: Photoionization (PID).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100  $\mu$ l.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5-ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

#### 5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids. Because of the toxicity of many of the compounds being analyzed, 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.

5.3.1 Place about 9 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100- $\mu$ l syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference

material falls directly into the alcohol without contacting the neck of the flask.

5.3.3 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.4 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 µl of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25-µl Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after one hour unless preserved, stored, and sealed according to 6.1 and 6.3.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 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. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain 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 min.

6.4 Sample preservation: Non-sterile samples containing aromatic hydrocarbons cannot be stored longer than 4 hr because of biological degradation. Samples can be stabilized by adding free chlorine or by adjusting the pH to less than 2 with 1:1 hydrochloric acid. However, free chlorine will react with styrene and 2,3-benzofuran. Therefore, if styrene or 2,3-benzofuran are to be determined in chlorinated water, the sample must be dechlorinated with sodium thiosulfate at the rate of 1 mg/ppm of free chlorine. Once dechlorinated, the sample pH must be adjusted to less than 2 with 1:1 hydrochloric acid. If chemical preservation is employed, the preservative is also added to the blanks.

6.5 All samples must be analyzed within 14 days of collection.

## 7.0 Procedures

7.1 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: The carrier gas is helium at a flow rate of 30 ml/min. The temperature program sequences are as follows: for lower boiling compounds, operate at 50° C isothermal for 2 min, then program at 6° C/min to 90° C

and hold until all compounds have eluted. For a higher boiling range of compounds, operate at 50° C isothermal for 2 min, then program at 3°/min to 110° C and hold until all compounds have eluted. Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para, meta, and ortho aromatic isomers.

Column 2: The carrier gas is helium at a flow rate of 30 ml/min. The temperature program sequence is as follows: 40° C isothermal for 2 min, then 2°/min to 100° C and hold until all compounds have eluted. Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, since the resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.2 Calibration. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Section 7.1.

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

#### 7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0 µl of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25-µl syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the

average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

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

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured

$A_{iS}$  = Response for the internal standard

$C_{iS}$  = Concentration of the internal standard

$C_S$  = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

### 7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. An example of the separation achieved by Column 2 is shown in Figure 2.

7.3.3 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be

TABLE 1. RETENTION TIMES FOR SOME AROMATIC VOLATILE ORGANICS

Compound	Retention time (min)	Method detection limit <sup>a</sup> (µg/l)
Benzene	3.33	0.2
Chlorobenzene	9.17	0.2
1,4-Dichlorobenzene	16.8	0.3
1,3-Dichlorobenzene	18.2	0.4
1,2-Dichlorobenzene	25.9	0.4
Toluene	5.75	0.2
Ethyl Benzene	8.25	0.2
Xylenes		

Column: 6-ft x 1/8-in. column packed with 1.75% Bentone 34 and 5% SP-2100 on Supelcoport 100/200.

<sup>a</sup>Using purge-and-trap Method 5030. See also Section 8.3.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses	Matrix types
Benzene	91	10.0	0.5-9.7	21	3
Chlorobenzene	97	9.4	0.5-100	21	3
1,2-Dichlorobenzene	104	27.7	0.5-10.0	21	3
1,3-Dichlorobenzene	97	20.0	0.5-4.8	21	3
1,4-Dichlorobenzene	120	20.4	0.5-10.0	21	3
Ethylbenzene	98	12.4	0.5-9.9	21	3
Toluene	77	12.1	0.5-100	21	3

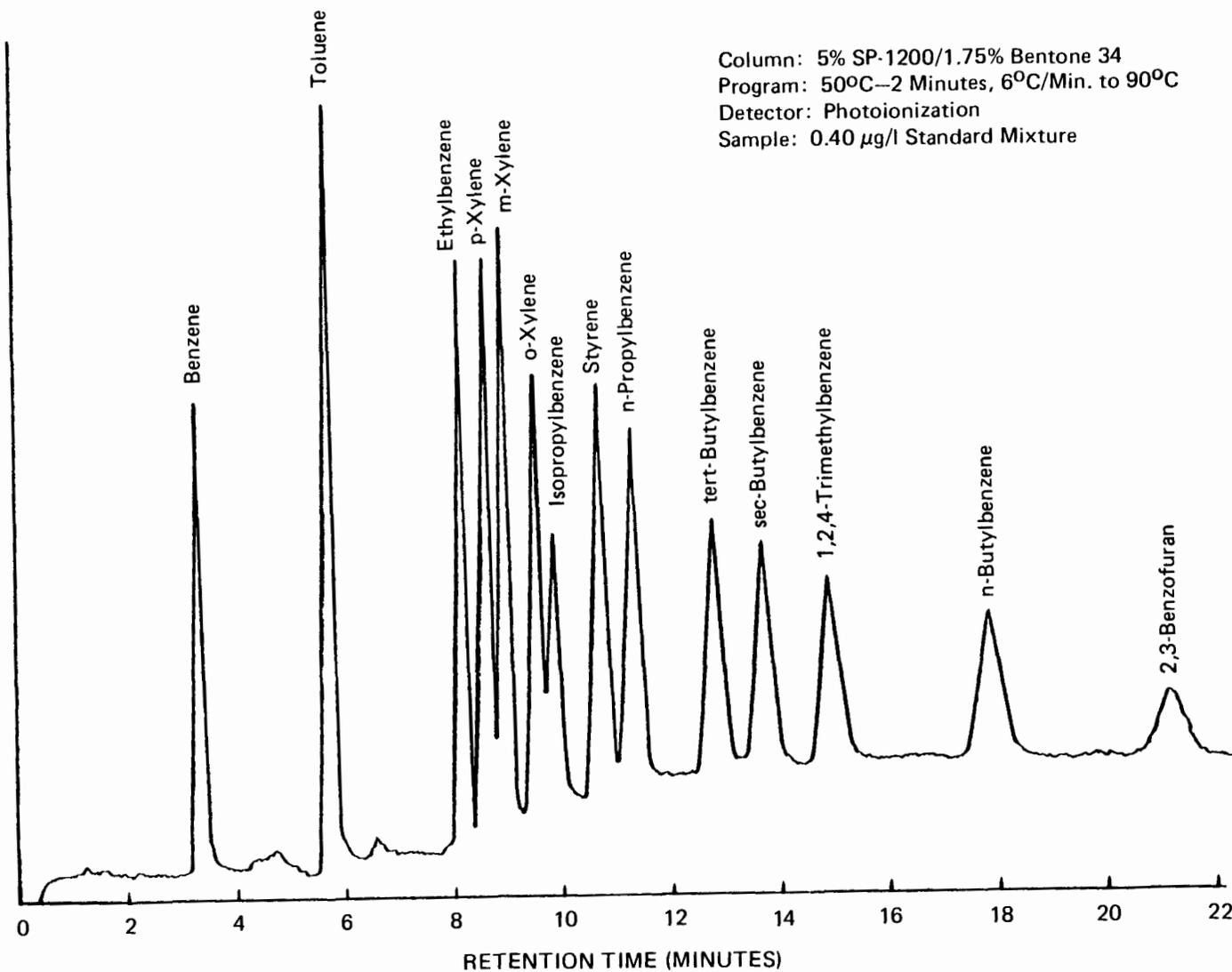


Figure 1. Chromatogram of aromatic volatile organics (column 1 conditions).

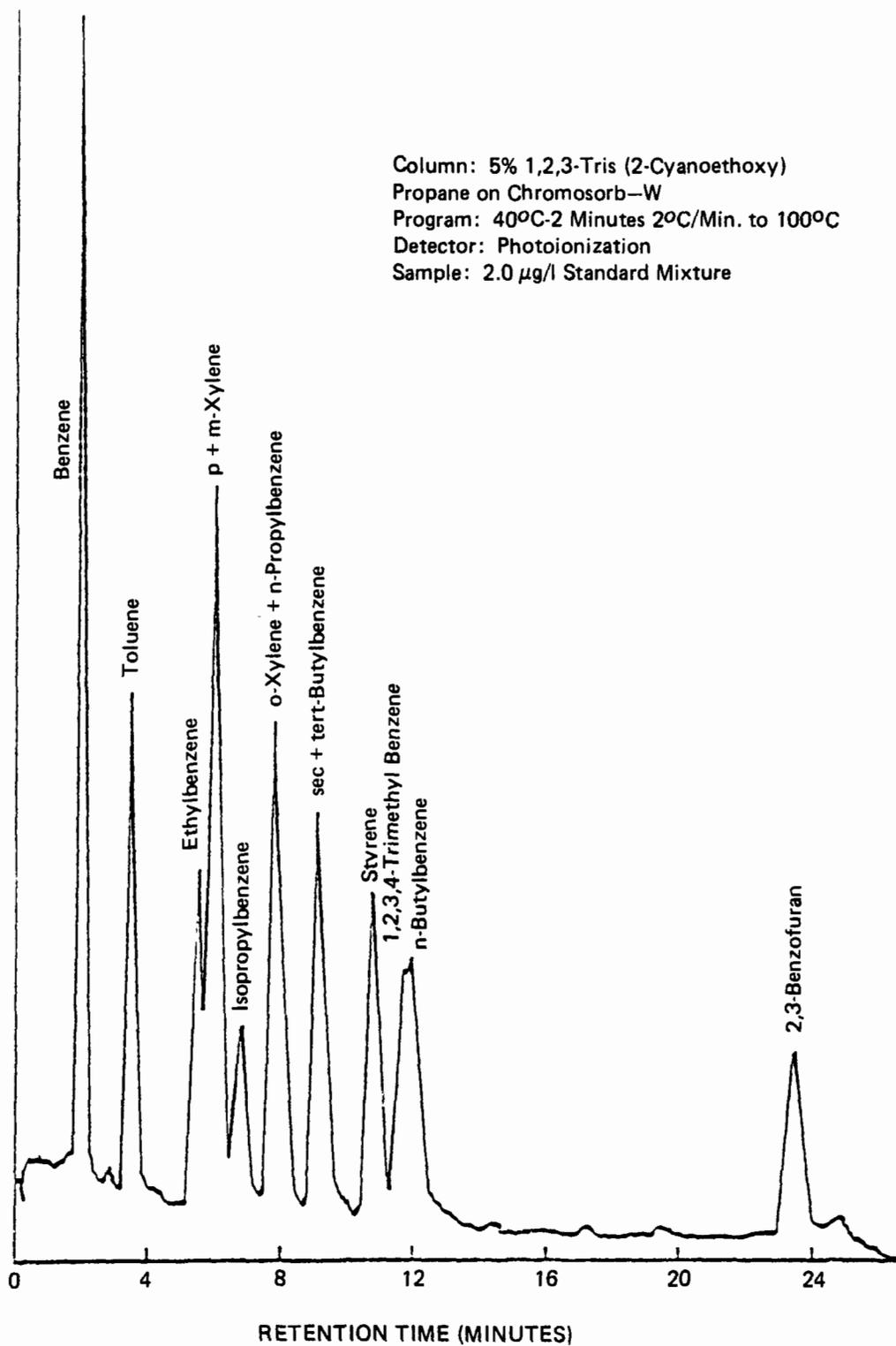


Figure 2. Chromatogram of aromatic volatile organics (column 2 conditions).

increased. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

## 9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
3. Dowty, B.J., S.R. Antoine, and J.L. Laseter. 1979. Quantitative and qualitative analysis of purgeable organics by high resolution gas chromatography and flame ionization detection. In: Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35.
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).

## METHOD 8030

### ACROLEIN, ACRYLONITRILE, ACETONITRILE

#### 1.0 Scope and Application

1.1 Method 8030 is used to determine the concentration of three volatile organic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8030 is used to detect the following substances:

Acrolein (Propenal)  
Acrylonitrile  
Acetonitrile

1.2 This method is recommended for use by, or under the supervision of, analysts experienced in the operation of gas chromatographs and in the interpretation of chromatograms.

#### 2.0 Summary of Method

2.1 Method 8030 provides chromatographic conditions for the detection of certain halogenated volatile organic compounds. Waste samples can be analyzed using direct injection, the headspace method (Method 5020) or the purge-and-trap method (Method 5030). Groundwater samples should be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

#### 3.0 Interferences

3.1 Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

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

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3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

### 4.0 Apparatus and Materials

4.1 Vial with cap: 40-ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C before use.

4.2 Septum: Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105° C for 30 min before use. NOTE: Do not heat the TFE seals for extended periods of time (i.e., more than 1 hr) because the silicone layer slowly degrades at 105° C.

4.3 Sample introduction apparatus for Methods 5020 and 5030.

4.4 Gas chromatograph: Analytical system complete with programmable gas chromatograph suitable for on-column injection or purge-and-trap sample introduction and all required accessories, including FID, column supplies, recorder, and gases. A data system for measuring peak area is recommended.

4.5 GC column: 6-ft x 1/8-in. stainless steel or 6-ft x 1/4-in. glass column packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.6 Detector: Flame ionization (FID).

4.7 Syringes: 5-ml glass hypodermic with Luerlok top (2 each).

4.8 Microsyringes: 10, 25, 100 µl.

4.9 Two-way syringe valve with Luer ends (3 each).

4.10 Syringe: 5-ml, gas-tight with shutoff valve.

4.11 Bottle: 15-ml screw-cap, with teflon cap liner.

## 5.0 Reagents

5.1 Activated carbon: Filtrasorb 200 (Calgon Corp.) or equivalent.

5.2 Organic-free water: Generated by passing tap water through a carbon filter bed containing about 1 lb of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 min. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for 1 hr.

5.3 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds being analyzed, 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.

5.3.1 Place about 8 ml of methyl alcohol into a 10-ml ground-glass-stoppered volumetric flask. Allow to stand about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100- $\mu$ l syringe, immediately add an amount of assayed reference material to the flask, then reweigh. Be sure that the reference material falls directly into the alcohol without contacting the neck of the flask.

5.3.3 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store at 4° C and protect from light.

5.3.4 Prepare fresh standards weekly for those compounds whose boiling point is less than or equal to 30° C and for the 2-chloroethyl-vinyl ether. All other standards must be replaced after 1 month, or sooner if comparison with check standards indicate a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the prepared aqueous calibration standards will completely bracket the working range of

the analytical system. Secondary dilution standards must be stored with zero headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Quality control check standards, available from the EPA's Environmental Monitoring and Support Laboratory in Cincinnati, can be used to determine the accuracy of calibration standards.

5.5 Calibration standards: In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20  $\mu$ l of alcoholic standards into 100 ml of reagent water.

5.5.2 Use a 25- $\mu$ l Hamilton 702N microsyringe or equivalent. (Variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water.)

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 For standards prepared in 500- or 1,000-ml flasks, discard the contents contained in the neck of the flask. Fill the sample syringe from the standard solution contained in the expanded area of the flask.

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr unless stored and sealed as stipulated in Sections 6.1 and 6.3.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers (see Apparatus, Sections 4.1 and 4.2) having a total volume of at least 25 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. Solid and semisolid samples are to be taken in the same way. Assure that no solid material interferes with sealing of the glass vial. Maintain the hermetic seal on the sample bottle until time of analysis.

6.2 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to

laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle attached or with no needle. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the enclosed end of the barrel of a glass hypodermic syringe.

6.3 The samples must be iced or refrigerated from the time of collection until extraction. If the sample may contain free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm  $\text{Cl}_2$ ) 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 min.

6.4 All samples must be analyzed within 14 days of collection.

## 7.0 Procedures

7.1 The recommended gas chromatographic column and operating conditions for the instrument are: Set helium gas flow at 45 ml/min flow rate. Set column temperature at 80° C for 5 min, then program an 8° C/min temperature rise to 150° C and until all compounds elute.

### 7.2 Calibration

7.2.1 By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1  $\mu\text{g}$  for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.2.2) or the internal standard technique (Section 7.2.3).

#### 7.2.2 External standard calibration procedure

7.2.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter by carefully adding 20.0  $\mu\text{l}$  of one or more secondary dilution standards to 100, 500, or 1,000 ml of reagent water or the matrix under study. A 25- $\mu\text{l}$  syringe should be used for this operation. One of the external standards should be at a concentration near, but above, the method detection limit and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector. These aqueous standards must be prepared fresh daily.

7.2.2.2 Analyze each calibration standard according to the procedure being used (direct aqueous injection, headspace, or

purge-and-trap) and tabulate peak height or area responses against the concentration in the standard. The results can be used to prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (less than 10% relative standard deviation), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that compound.

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

7.2.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest as described in Section 7.2.2.1.

7.2.3.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4.

7.2.3.3 Analyze each calibration standard according to appropriate methods (direct injection, 5020, 5030), adding the internal standard spiking solution directly to an aliquot of the sample or, in the case of purge-and-trap, to the syringe. Tabulate peak height or area responses against concentration for each compound and internal standard, and calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured

$A_{iS}$  = Response for the internal standard

$C_{iS}$  = Concentration of the internal standard

$C_S$  = Concentration of the parameter to be measured

If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.2.3.4 The working calibration curve or RF must be verified on each working day by measuring one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, either the test must be repeated using a fresh calibration standard, or a new calibration curve must be prepared for that compound.

### 7.3 Gas chromatographic analysis

7.3.1 Introduce volatile compounds to the gas chromatograph using direct injection, headspace (Method 5020), or purge-and-trap (Method 5030).

7.3.2 Calibrate the system immediately prior to conducting any analysis and recheck for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be

increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min)	Method detection limit <sup>a</sup> ( $\mu\text{g/l}$ )
Acrolein	8.2	0.6
Acrylonitrile	9.8	0.5

<sup>a</sup>Method detection limit is based upon recovery of 5.0  $\mu\text{g/l}$  dose into tap water.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
Acrolein	96	11.6	20	7	1
Acrylonitrile	107	5.6	20	7	1

## 9.0 References

1. Bellar, T.A., and J.J. Lichtenberg. 1974. J. Amer. Water Works Assoc. 66(12):739-744.
2. Bellar, T.A., and J.J. Lichtenberg. 1979. Semi-automated headspace analysis of drinking waters and industrial waters for purgeable volatile organic compounds. In: Van Hall (ed.), Measurement of organic pollutants in water and wastewater. ASTM STP 686, pp. 108-129.
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).
4. Going, John, et al. 1979. Environmental monitoring near industrial sites - Acrylonitrile. EPA Report No. 560/6-79-003.

## METHOD 8040

### PHENOLS

#### 1.0 Scope and Application

1.1 Method 8040 is used to determine the concentration of various phenolic compounds in groundwater, liquid, and solid matrices. Specifically, Method 8040 may be used to detect the following substances:

Phenol	4-Chloro-3-methylphenol
2-Chlorophenol	2,4-Dimethylphenol
2,4-Dichlorophenol	2-Nitrophenol
2,6-Dichlorophenol	4-Nitrophenol
Trichlorophenols	2,4-Dinitrophenol
Tetrachlorophenols	2-sec-Butyl-4,6-dinitrophenol (DNBP)
Pentachlorophenol	2-Cyclohexyl-4,6-dinitrophenol
Cresol (methyl phenols)	2-Methyl-4,6-dinitrophenol
4,6-Dinitro-o-cresol	

1.2 Method 8040 is recommended for use only by, or under the close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8040 provides chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques. Water and groundwater samples are extracted at a pH of less than or equal to 2 with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a pH of less than or equal to 2 with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID). An aliquot of each sample must be spiked with standards to determine the spike recovery and the limits of detection for that particular sample.

2.2 Method 8040 also provides for the preparation of pentafluorobenzyl-bromide (PFB) derivatives with additional cleanup procedures for electron capture gas chromatography to aid the analyst in the elimination of interferences.

2.3 The sensitivity of Method 8040 usually depends on the level of interferences rather than on instrumental limitations. The detection limits listed in Table 1 for some phenols represent sensitivities that can be achieved in wastewaters in the absence of interferences. However, in typical waste samples, detection limits would be higher. The use of derivatization cleanup, if necessary, will also increase detection limits.

### 3.0 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 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 samples will vary considerably from source to source depending upon the waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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.

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS<sup>a</sup>

Compound	Retention time	Detection limit ( $\mu\text{g/l}$ ) <sup>b</sup>
2-Chlorophenol	1.70	0.31
2-Nitrophenol	2.00	0.45
Phenol	3.01	0.14
2,4-Dimethylphenol	4.03	0.32
2,4-Dichlorophenol	4.30	0.39
2,4,6-Trichlorophenol	6.05	0.64
4-Chloro-3-methylphenol	7.50	0.36
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
Pentachlorophenol	12.42	7.4
4-Nitrophenol	24.25	2.8

<sup>a</sup>Taken from Reference 1.

<sup>b</sup>Detection limit is calculated from the minimum detectable GC response being equal to 5 times the GC background noise, assuming a 10-ml final extract volume of the 1-liter sample extract, assuming a GC injection of 5 ml.

Fortified samples should be analyzed to validate the accuracy of the analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1  $\mu\text{g/g}$  of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 when analyzing groundwater samples.

#### 4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. Pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 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.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs (Kontes K-662750-0012).

4.2.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ \text{C}$ ). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections 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.

4.5 Chromatographic column: 10-mm I.D. by 100-mm length, with Teflon stopcock.

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4.6 Reaction vial: 20-ml, with Teflon-lined cap.

#### 5.0 Reagents

##### 5.1 Preservatives

5.1.1 Sodium hydroxide: (ACS) 10 N in distilled or distilled, deionized water.

5.1.2 Sulfuric acid: (1:1) Mix equal volumes of conc. H<sub>2</sub>SO<sub>4</sub> (ACS) with distilled or distilled, deionized 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 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g 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.

5.5 Sulfuric acid: (ACS) 1 N in distilled water.

5.6 Potassium carbonate: (ACS) powdered.

5.7 Pentafluorobenzyl bromide (α-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 g 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 desiccator.

## 6.0 Sample Collection, Preservation, and Handling

6.1 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.

6.2 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 ppm free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid solution or 10 N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

### 7.1 Sample preparation

#### 7.1.1 Extraction

Extract water samples at a pH of less than or equal to 2 with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Solid samples are extracted at a pH of less than or equal to 2 with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. An aliquot of each sample must be spiked with standards to determine the percent recovery and the limits of detection for that sample.

#### 7.1.2 Derivatization

If interferences prevent measurement of the peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.1.2.1 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.

7.1.2.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

7.1.2.3 Cap the mixture and heat it for 4 hr at 80° C in a hot water bath.

7.1.2.4 Remove the solution from the hot water bath and allow it to cool.

7.1.2.5 Add 10 ml hexane to the reaction vial and shake vigorously for 1 min. Add 3.0 ml distilled, deionized water to the reaction vial and shake for 2 min.

7.1.2.6 Decant organic layer into a concentrator tube and cap with a glass stopper.

7.1.2.7 Pack a 10-mm I.D. chromatographic column with 4.0 g of activated silica gel. After settling the silica gel by tapping the column, add about 2 g of anhydrous sodium sulfate to the top.

7.1.2.8 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 that contains the derivatized sample of 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 some phenolic derivatives are shown in Table 2. Fractions may be combined as desired, depending upon the specific phenols of interest or level of interferences.

7.2 The recommended gas chromatographic columns and operating conditions for the instruments are:

Column 1 conditions: Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 6-ft long x 2-mm I.D. glass column with nitrogen carrier gas at 30 ml/min flow rate. Column temperature is 80° C at injection, and then programmed immediately at 8° C/min to a 150° C final temperature.

Column 2 conditions: Chromosorb W-AW-DMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8-m long x 2.0-mm I.D. glass column with 5% methane/95% argon carrier gas at 30 ml/min flow rate. Column temperature is 200° C.

TABLE 2. ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES<sup>a</sup>

Parent compound	Method detection limit ( $\mu\text{g}/\text{l}$ )	Retention time (min) <sup>b</sup>	Percent recovery by fraction				
			1	2	3	4	5
2-Chlorophenol	0.58	3.3			90	over 1	90
2-Nitrophenol	0.77	9.1				9	
Phenol	2.2	1.8			90	10	
2,4-Dimethylphenol	0.63	2.9			95	7	
2,4-Dichlorophenol	0.68	5.8			95	over 1	
2,4,6-Trichlorophenol	0.58	7.0		50	50		
4-Chloro-2-methylphenol	1.8	4.8			84	14	
Pentachlorophenol	0.59	28.8		75	20		
4-Nitrophenol	0.70	14.0				over 1	90
(2,4-Dinitrophenol)		46.9					
(2-Methyl-4,6-dinitrophenol)		36.6					

<sup>a</sup>Taken from Reference 1.

<sup>b</sup>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.

### 7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.2. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to  $1 \mu\text{g}$  for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

#### 7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{is}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_s$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_s/A_{is}$  against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

## 7.4 Gas chromatographic analysis

7.4.1 Phenols are to be analyzed on a gas chromatograph equipped with a flame ionization detector according to column 1 conditions (Section 7.2). Table 1 summarizes estimated retention times and sensitivities that should be achieved by this method for clean water samples. Detection limits for a typical waste sample would be significantly higher. If peak detection is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to column 2 conditions (Section 7.2). Table 2 summarizes estimated retention times as well as percent recoveries for the fractionation procedure.

7.4.2 Inject 2 to 5  $\mu\text{l}$  of the sample extract using the solvent flush technique. Smaller (1.0  $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.4.3 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of sample preparation and measurement. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

## 9.0 References

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.)

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
4-Chloro-3-methylphenol	82	15.0	0.70-3.5	21	3
2-Chlorophenol	67	14.8	0.74-3.7	21	3
2,4-Dichlorophenol	74	11.4	1.03-5.2	21	3
2,4-Dimethylphenol	51	14.0	0.82-4.1	21	3
2,4-Dinitrophenol	74	16.5	28.7	14	2
2-Methyl-4,6-dinitrophenol	86	12.4	34.6	21	3
2-Nitrophenol	67	12.9	0.80-4.0	21	3
4-Nitrophenol	45	7.9	15.9	21	3
Pentachlorophenol	79	8.8	21.0	21	3
Phenol	41	8.4	0.76-3.8	21	3
2,4,6-Trichlorophenol	71	14.5	1.20-6.0	21	3

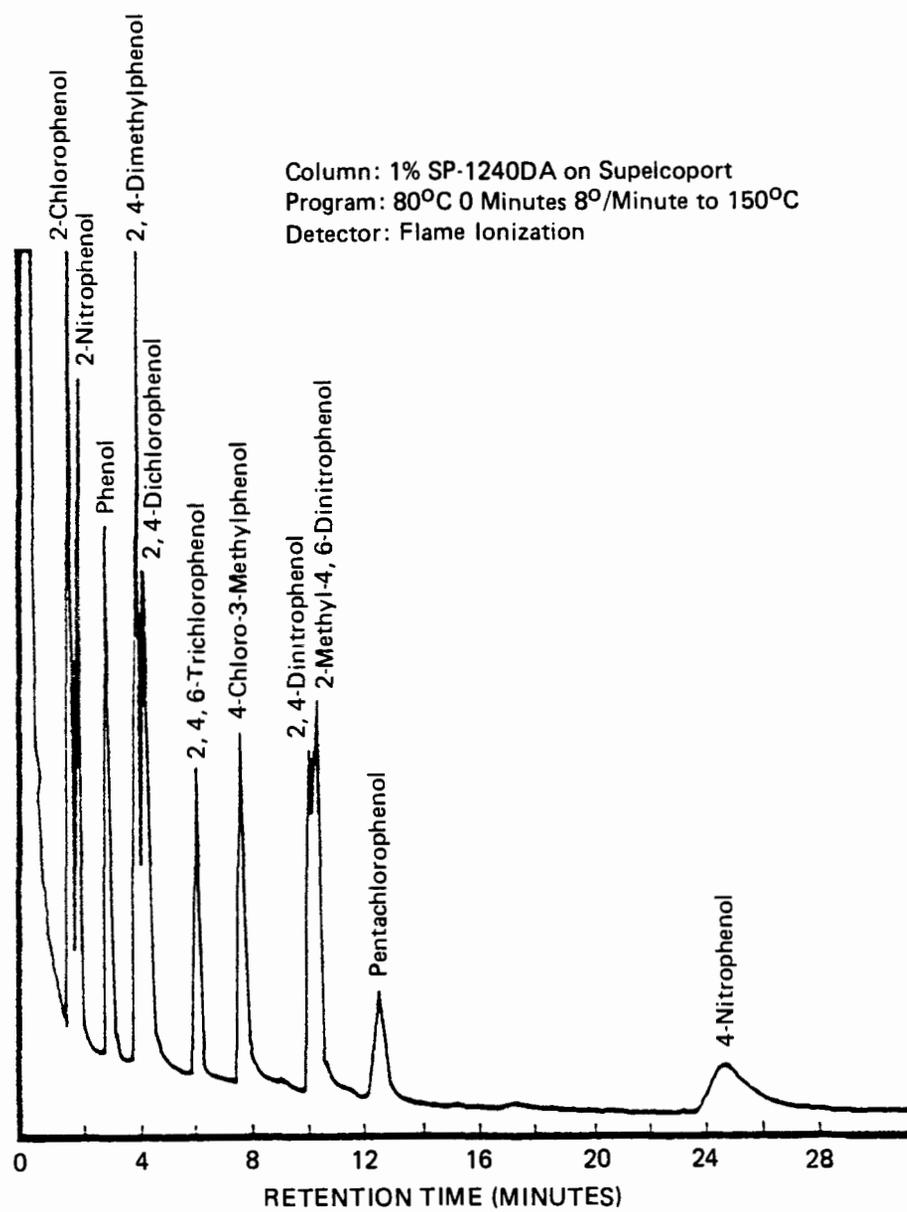


Figure 1. Gas chromatogram of phenols.

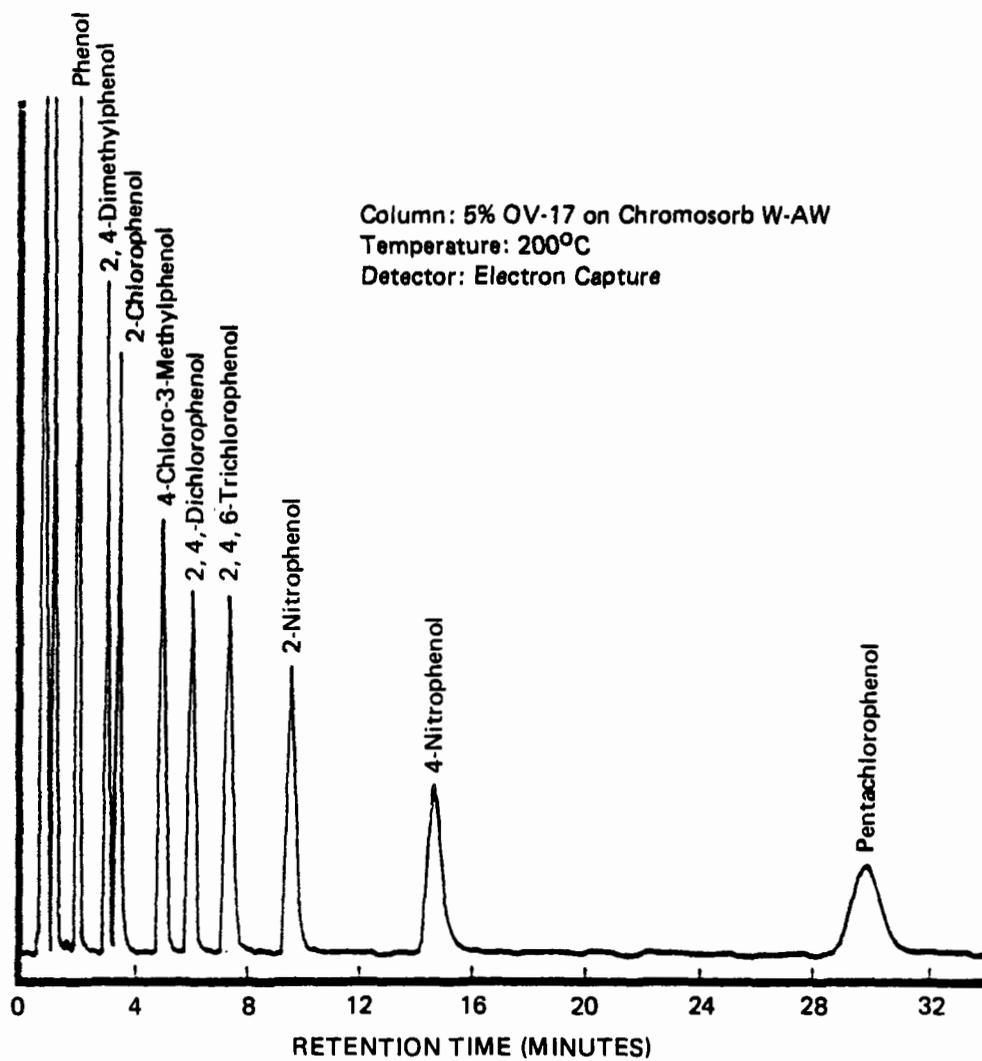


Figure 2. Gas chromatogram of PFB derivatives of phenols.

## METHOD 8060

### PHTHALATE ESTERS

#### 1.0 Scope and Application

1.1 Method 8060 is used to determine the concentration of phthalate esters in groundwater, liquid, and solid sample matrices. Specifically, Method 8060 may be used to detect the following substances:

- Benzyl butyl phthalate
- Bis(2-ethylhexyl)phthalate
- Di-n-butyl phthalate
- Di-n-octyl phthalate
- Diethyl phthalate
- Dimethyl phthalate

1.2 The applicability of Method 8060 to other phthalate compounds can be determined by means of a spike recovery study.

1.3 Method 8060 is recommended for use only by, or under the close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8060 provides cleanup and gas chromatographic conditions for the detection of ppb levels of phthalate esters. Prior to use of this method, appropriate sample extraction techniques must be used. Water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a neutral pH with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). Groundwater samples should be determined by ECD. An aliquot of each sample will be spiked with standards to determine percent recovery and the limits of detection for that sample.

2.2 The sensitivity of Method 8060 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits in groundwater should be approximately the same. Detection limits for a typical waste sample would be significantly higher.

#### 3.0 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 these materials must therefore 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 waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

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 min. Some high boiling materials, such as PCB's, 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 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 analysis. Plastics in particular must be avoided 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.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.6 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 when analyzing groundwater samples.

TABLE 1. GAS CHROMATOGRAPHY OF PHTHALATE ESTERS<sup>a</sup>

Compound	Retention time (min)		Detection limit ( $\mu\text{g/l}$ )	
	Col. 1 <sup>b</sup>	Col. 2 <sup>c</sup>	ECD	FID
Dimethyl phthalate	2.03	0.95	0.29	19
Diethyl phthalate	2.82	1.27	0.49	31
Di-n-butyl phthalate	8.65	3.50	0.36	14
Benzyl butyl phthalate	*6.94	**5.11	0.34	15
Bis(2-ethylhexyl) phthalate	*8.92	**10.5	2.0	20
Di-n-octyl phthalate	*16.2	**8.0	3.0	31

<sup>a</sup>Taken from Reference 1.

<sup>b</sup>Column 1: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with carrier gas at 60 ml/min flow rate. Column temperature is 180° C except where \* indicates 220° C. Under these conditions retention time of Aldrin is 5.49 min at 180° C and 1.84 min at 220° C.

<sup>c</sup>Column 2: Supelcoport 100/120 mesh with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with carrier gas at 60 ml/min flow rate. Column temperature is 200° C except where \*\* indicates 220° C. Under these conditions retention time of Aldrin is 3.18 min at 200° C and 1.46 min at 220° C.

#### 4.0 Apparatus and Materials

4.1 2000-ml separatory funnel with Teflon stopcock.

4.2 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 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.

4.3.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs (Kontes K-662750-0012).

4.3.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

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4.3.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^{\circ}$  C). The bath should be used in a hood.

4.5 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.

4.6 Chromatography column: 300-mm long x 10-mm I.D., with coarse disc at bottom and Teflon stopcock (Kontes K-420540-0213 or equivalent).

## 5.0 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.  $\text{H}_2\text{SO}_4$  with distilled water.

5.2 Methylene chloride: Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at  $400^{\circ}$  C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of  $1.00 \mu\text{g}/\mu\text{l}$  by dissolving 0.100 g 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, NY 10523.)

5.6 Florisil: PR grade (60/100 mesh); purchase-activated at  $1250^{\circ}$  F; store in glass containers 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.

## 6.0 Sample Collection, Preservation, and Handling

6.1 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.

6.2 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 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hr of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

7.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. An aliquot of each sample should be spiked with standards to determine the percent recovery and the limit of detection for that sample.

### 7.2 Cleanup and separation

7.2.1 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 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 in 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 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches

about 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 min 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.

#### 7.2.2 Florisil column cleanup for phthalate esters

7.2.2.1 Place 100 g of Florisil into a 500-ml beaker and heat for approximately 16 hr 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 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

7.2.2.2 Place 10 g of this Florisil preparation into a 10-mm I.D. chromatography column and tap the column to settle the Florisil. Add 1 cm of anhydrous sodium sulfate to the top of the Florisil.

7.2.2.3 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 to complete the transfer.

7.2.2.4 Just prior to exposure of the sodium sulfate layer to the air, add 40 ml of hexane and continue the elution of the column. Discard this hexane eluate.

7.2.2.5 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/min 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.

#### 7.2.3 Alumina column cleanup for phthalate esters

7.2.3.1 Place 100 g of alumina into a 500-ml beaker and heat for approximately 16 hr 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 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

7.2.3.2 Place 10 g of this alumina preparation into a 10-mm I.D. chromatography column and tap the column to settle the alumina. Add 1 cm of anhydrous sodium sulfate to the top of the alumina.

7.2.3.3 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.

7.2.3.4 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.

7.2.3.5 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/min 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.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm-long x 4-mm I.D. glass column with carrier gas at 60 ml/min flow rate. Column temperature is 180° C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 3% OV-1 in a 180-cm-long x 4-mm I.D. glass column with carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

#### 7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.3. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

##### 7.4.2 External standard calibration procedure

7.4.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isoctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected

range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.4.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.4.3.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{iS}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_S$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.4.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

## 7.5 Gas chromatographic analysis

7.5.1 Either a flame ionization or electron capture detector may be used; however, the electron capture detector provides substantially better sensitivity.

7.5.2 Inject 2 to 5  $\mu\text{l}$  of the sample extract using the solvent flush technique. Smaller (1.0  $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.5.3 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.5.4 If peak detection is prevented by the presence of interferences, further cleanup is required. 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.

7.5.5 Examples of chromatograms for phthalate esters detected with an electron capture detector are shown in Figures 1 and 2.

## 8.0 Quality Control

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware

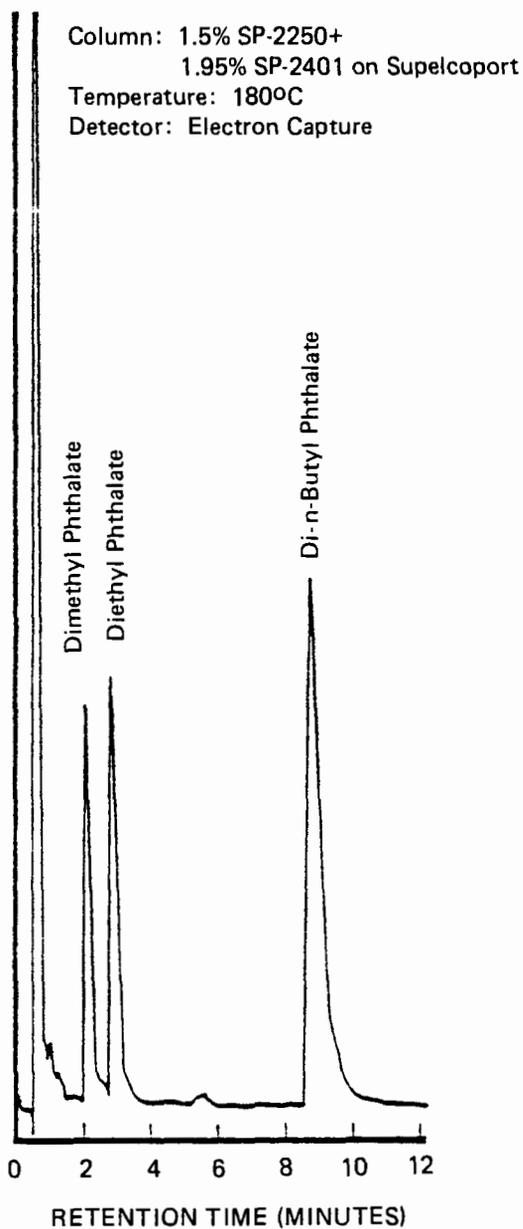


Figure 1. Gas chromatogram of phthalates (example 1).

Column: 1.5% SP-2250+  
1.95% SP-2401 on Supelcoport  
Temperature: 180°C  
Detector: Electron Capture

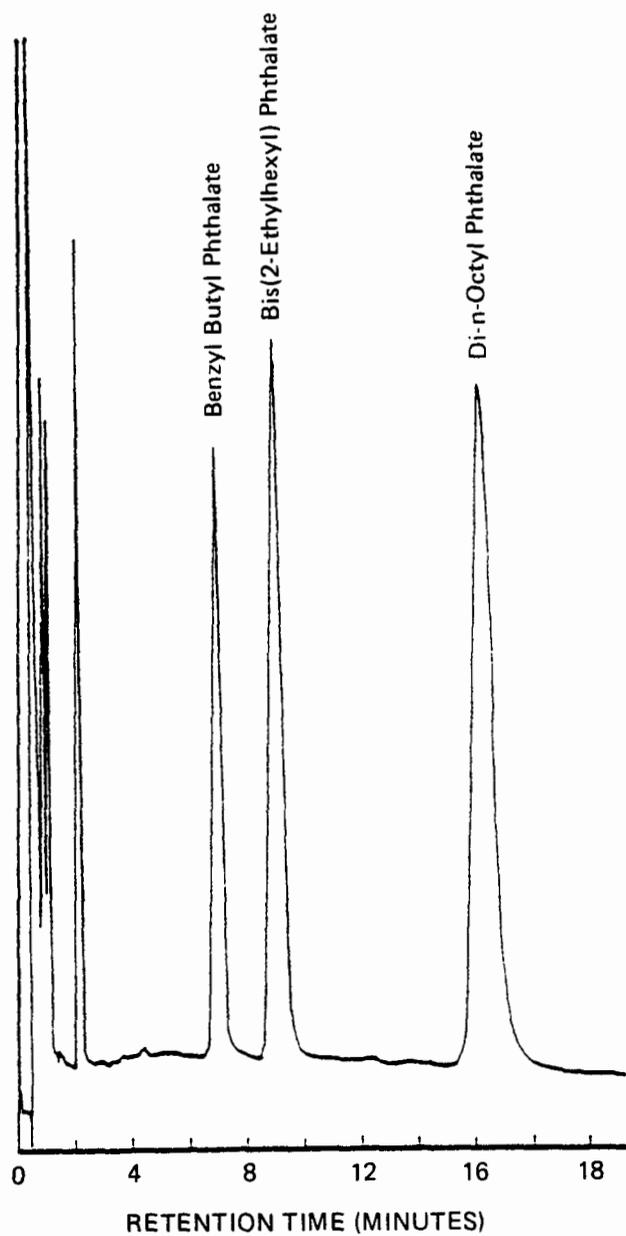


Figure 2. Gas chromatogram of phthalates (example 2).

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.

8.2 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 waste samples should be analyzed to validate the accuracy of the analysis. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
Bis(2-ethylhexyl) phthalate	85	4.2	24-1000	24	4
Butyl benzyl phthalate	82	6.5	3-100	24	4
Di-n-butyl-phthalate	80	6.2	20-1500	24	4
Diethyl phthalate	94	1.3	15-50	18	3
Dimethyl phthalate	94	3.4	15-50	18	3
Di-n-octyl-phthalate	86	4.9	40-150	24	4

9.0 References

1. 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).

## METHOD 8080

### ORGANOCHLORINE PESTICIDES AND PCB'S

#### 1.0 Scope and Application

1.1 Method 8080 is used to determine the concentration of certain organochlorine pesticides and polychlorinated biphenyls (PCB's) in ground-water, liquid, and solid sample matrices. Specifically, Method 8080 may be used to detect the following substances:

Aldrin	Endrin aldehyde
$\alpha$ -BHC	Heptachlor
$\beta$ -BHC	Heptachlor epoxide
$\gamma$ -BHC	Kepone
$\delta$ -BHC (Lindane)	Methoxychlor
Chlordane	Toxaphene
4,4'-DDD	PCB-1016
4,4'-DDE	PCB-1221
4,4'-DDT	PCB-1232
Dieldrin	PCB-1242
Endosulfan I	PCB-1248
Endosulfan II	PCB-1254
Endosulfan sulfate	PCB-1260
Endrin	

1.2 Method 8080 is recommended for use only by, or under the close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8080 provides cleanup and chromatographic conditions for the detection of ppb levels of organochlorine pesticides and PCB's. Prior to the use of this method, appropriate sample extraction techniques must be used. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or another halogen-specific detector. An aliquot of each sample will be spiked with standards to determine the spike recovery and the limits of detection for that particular sample. It is recommended that the analyst carefully select the compounds used in sample spiking to avoid coelution under the GC conditions given in Table 1. Aroclor 1221 will give minimal interference with the single component pesticides listed in Table 1. Chlordane and toxaphene may require individual spiked sample analysis to yield valid recovery data.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCB'S<sup>a</sup>

Parameter	Retention time (min)		Detection limit <sup>b</sup> ( $\mu\text{g/l}$ )
	Column 1 <sup>c</sup>	Column 2 <sup>d</sup>	
Aldrin	2.40	4.10	0.004
$\alpha$ -BHC	1.35	1.82	0.004
$\beta$ -BHC	1.90	1.97	0.006
$\omega$ -BHC	2.15	2.20	0.009
$\gamma$ -BHC (Lindane)	0.70	2.13	0.004
Chlordane	e	e	0.014
4,4'-DDD	7.83	9.08	0.012
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.004
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
PCB-1016	e	e	ND
PCB-1221	e	e	ND
PCB-1232	e	e	ND
PCB-1242	e	e	0.065
PCB-1248	e	e	ND
PCB-1254	e	e	ND
PCB-1260	e	e	ND

ND = not determined.

<sup>a</sup>Taken from reference 6.

<sup>b</sup>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 a 1-liter liquid extract, and assuming a GC injection of 5  $\mu\text{l}$ .

<sup>c</sup>Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

<sup>d</sup>Column 2 conditions: Supelcoport 100/200 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

<sup>e</sup>Multiple peak response.

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample may be significantly higher.

### 3.0 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 these materials must therefore 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 waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

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 min. Some high boiling materials, such as PCB's, 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 a microcoulometric or electrolytic conductivity detector.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should

be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

#### 4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated. 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.

4.2.2 Evaporative flask: 500 ml. Attach to concentrator tube with springs.

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Boiling chips: Extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron-capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatographic column: Pyrex, 400 mm x 25 mm O.D., with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

#### 5.0 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  $400^\circ$  C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of 1.00 µg/µl by dissolving 0.100 g 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 Mercury: Triple distilled.

5.6 Hexane: Pesticide residue analysis grade.

5.7 Isooctane (2,2,4-trimethyl pentane): Pesticide residue analysis grade.

5.8 Acetone: Pesticide residue analysis grade.

5.9 Diethyl ether: Nanograde, redistilled in glass if necessary.

5.9.1 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).

5.9.2 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.

5.10 Florisil: PR grade (60/100 mesh); purchase activated at 1250° F; store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at least 16 hr at 130° C in a foil-covered glass container.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in appropriately cleaned glass containers and the sampling bottle must not be prewashed with the 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.

6.2 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 hr 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.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

### 7.1 Sample preparation

7.1.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (3520). Extract solid samples with hexane:acetone (1:1) using either the Soxhlet extraction (Method 3540) or sonication procedures (Method 3550). Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. Each sample must be spiked to determine the % recovery and the limit of detection for that sample.

#### 7.1.2 Florisil column cleanup

7.1.2.1: Add a weight of Florisil (nominally 21 g), pre-determined by calibration (Section 7.3) 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. Packing the Florisil in a hexane slurry is an alternative method which has proven effective. 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. 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.

7.1.2.2 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 hexane (Fraction 2), into a second K-D flask. Perform the third elution using 200 ml of 50% ethyl ether in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 2.

7.1.2.3 Concentrate the eluates by standard K-D techniques, as described in the referenced extraction procedures, 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.

TABLE 2. DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCB'S USING FLORISIL COLUMN CHROMATOGRAPHY<sup>a</sup>

Parameter	Percent recovery by fraction <sup>b</sup>		
	1(6%)	2(15%)	3(50%)
Aldrin	100		
<u>α</u> -BHC	100		
<u>β</u> -BHC	97		
<u>γ</u> -BHC	98		
<u>δ</u> -BHC (Lindane)	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Heptachlor	100		
Heptachlor epoxide	100		
Methoxychlor	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		

<sup>a</sup>Taken from reference 1.<sup>b</sup>Eluting solvent composition given in Section 7.1.2.2.

7.2 Gas chromatography conditions. The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1 conditions: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

Column 2 conditions: Supelcoport 100/120 mesh coated with 3% OV-1 in a 180-cm long x 4-mm I.D. glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200° C.

### 7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

#### 7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Using injections of 2 to 5  $\mu\text{l}$  of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$\text{RF} = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{iS}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_S$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.3.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

7.3.4 Florisil standardization. The cleanup procedure described in Section 7.1.2 utilizes Florisil chromatography. Florisil from

different batches or sources may vary in absorption capacity. To determine the amount of Florisil to be used, the absorption capacity of each separate batch of Florisil is measured using lauric acid values (2). The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 g.

#### 7.4 Gas chromatographic analysis

7.4.1 Inject 2-5  $\mu\text{l}$  of the sample extract using the solvent flush technique. Smaller (1.0  $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.4.2 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. 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.

7.4.4 Examples of chromatograms for organochlorine pesticides are shown in Figures 1-5.

### 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 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 sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. The fortified samples should be carried through all stages of the sample preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

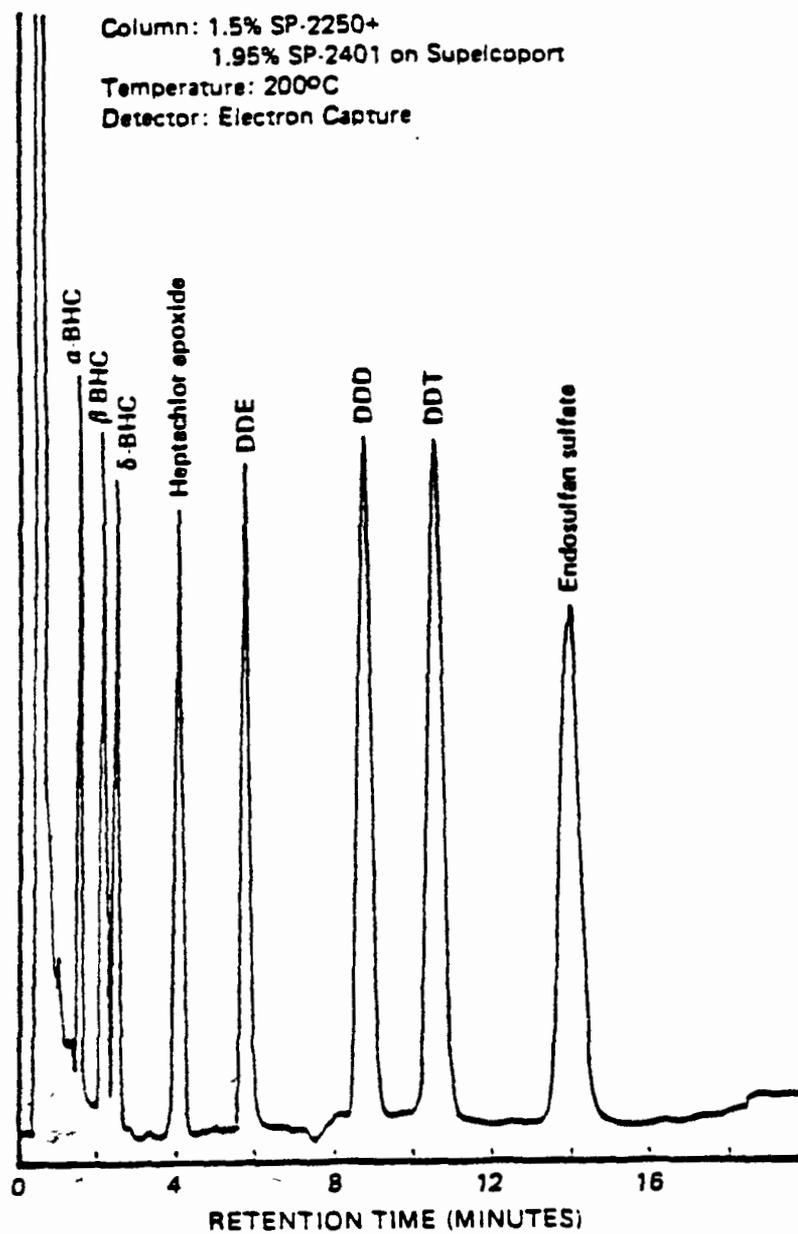


Figure 1. Gas chromatogram of pesticides.

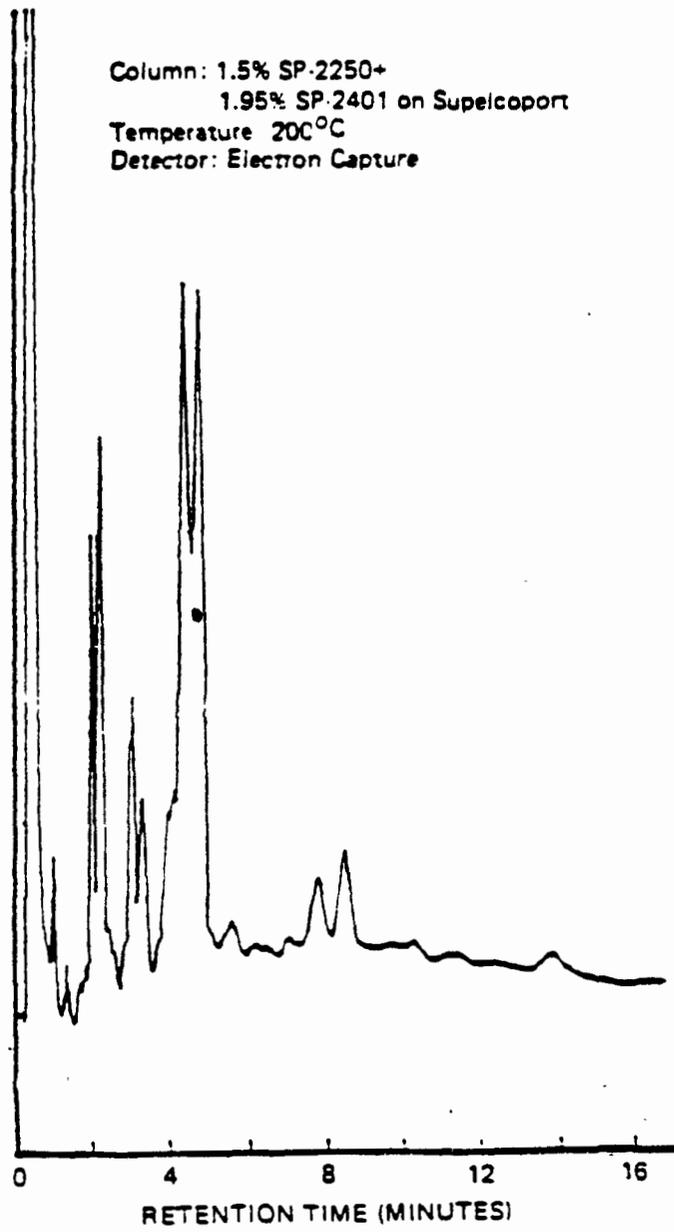


Figure 2. Gas chromatogram of chlordane.

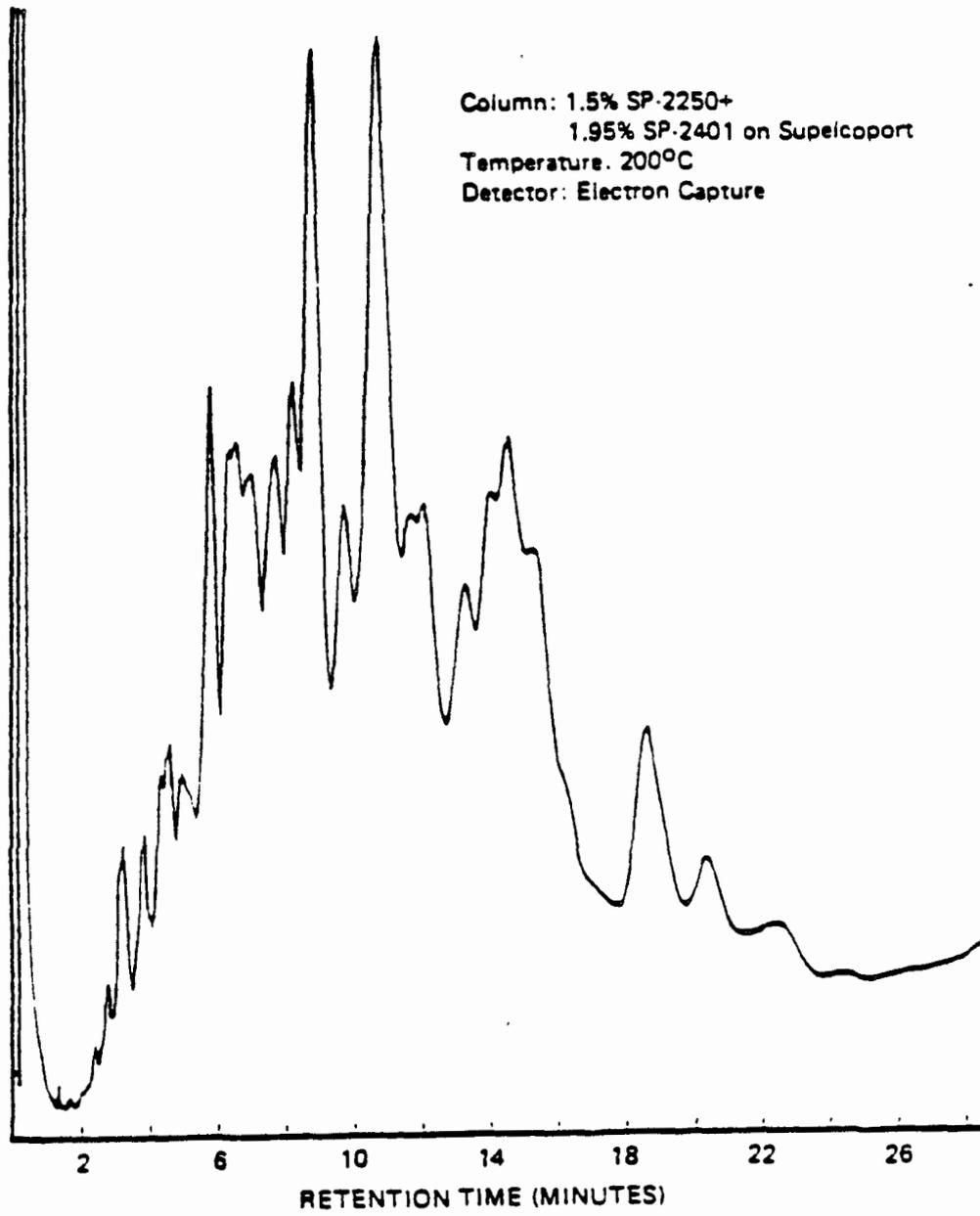


Figure 3. Gas chromatogram of toxaphene.

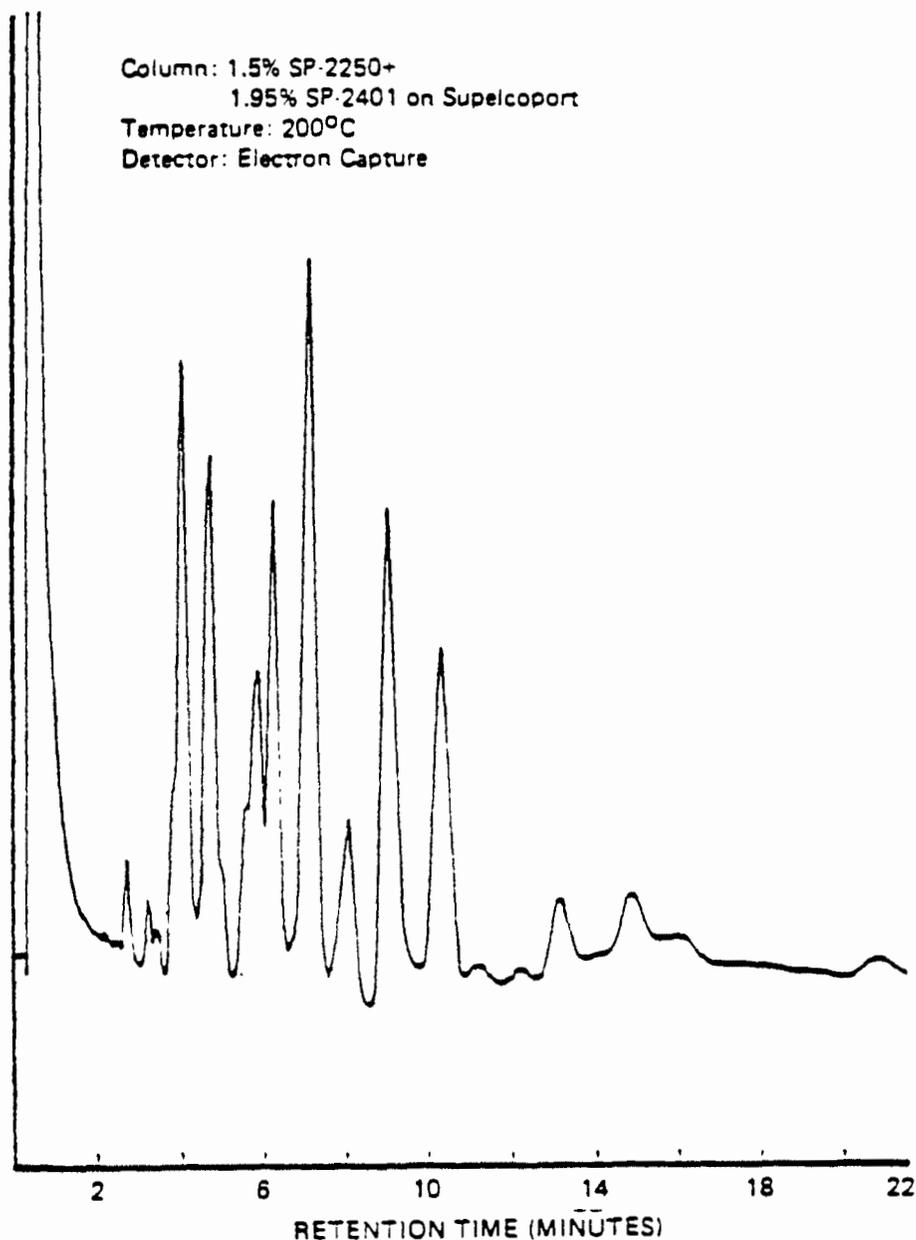


Figure 4. Gas chromatogram of PCB-1254.

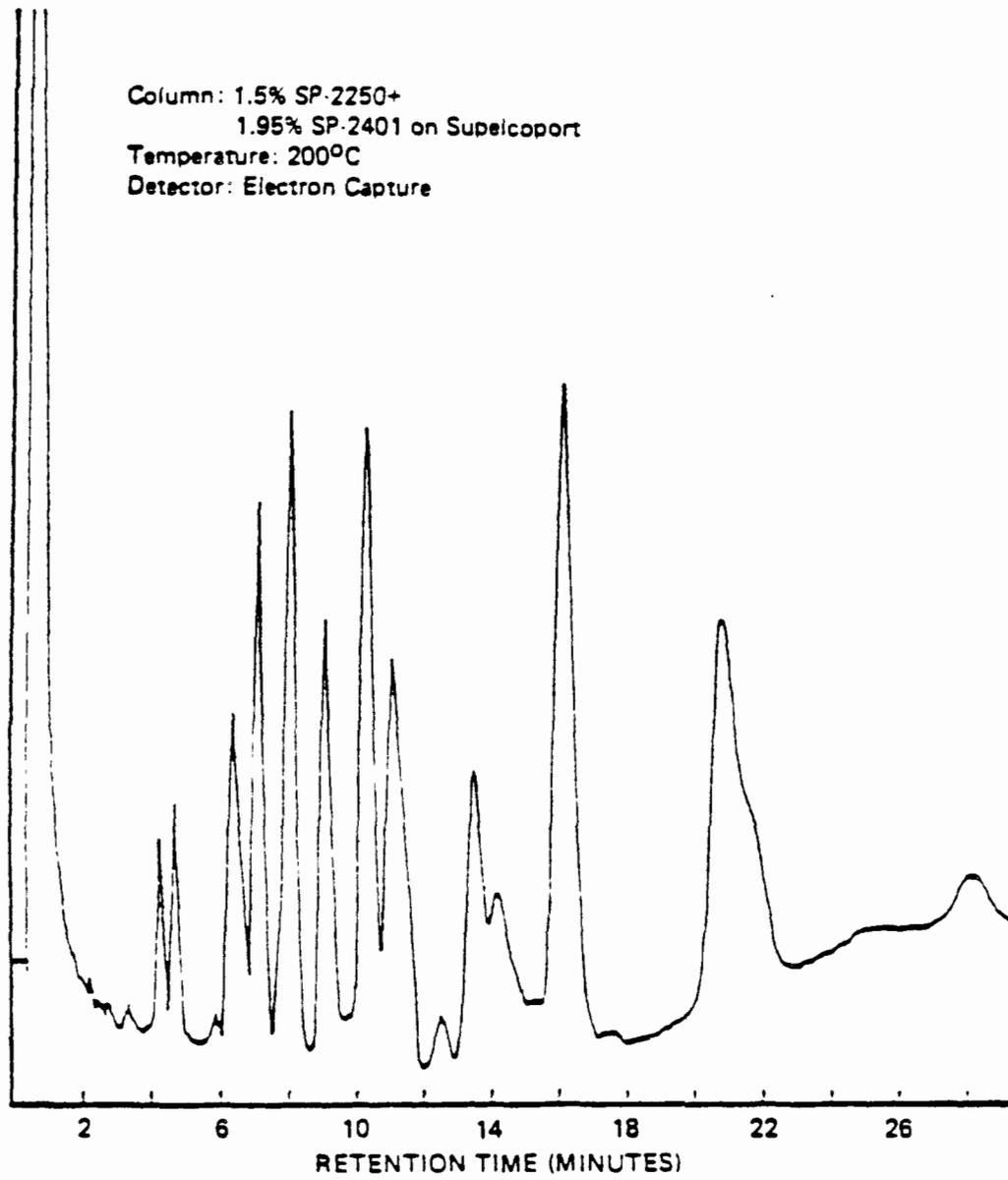


Figure 5. Gas chromatogram of PCB-1260.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
Aldrin	89	2.5	2.0	15	3
$\alpha$ -BHC	89	2.0	1.0	15	3
$\beta$ -BHC	88	1.3	2.0	15	3
$\gamma$ -BHC	86	3.4	2.0	15	3
$\delta$ -BHC (Lindane)	97	3.3	1.0	15	3
Chlordane	93	4.1	20	21	4
4,4'-DDD	92	1.9	6.0	15	3
4,4'-DDE	89	2.2	3.0	15	3
4,4'-DDT	92	3.2	8.0	15	3
Dieldrin	95	2.8	3.0	15	2
Endosulfan I	96	2.9	3.0	12	2
Endosulfan II	97	2.4	5.0	14	3
Endosulfan sulfate	99	4.1	15	15	3
Endrin	95	2.1	5.0	12	2
Endrin aldehyde	87	2.1	12	11	2
Heptachlor	88	3.3	1.0	12	2
Heptachlor epoxide	93	1.4	2.0	15	3
Toxaphene	95	3.8	200	18	3
PCB-1016	94	1.8	25	12	2
PCB-1221	96	4.2	55-100	12	2
PCB-1232	88	2.4	110	12	2
PCB-1242	92	2.0	28-56	12	2
PCB-1248	90	1.6	40	12	2
PCB-1254	92	3.3	40	18	3
PCB-1260	91	5.5	80	18	3

## 9.0 References

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. 1968. Variation of florisil activity: simple method for measuring absorbent capacity and its use in standardizing florisil columns. J. Assoc. Official Anal. Chem. 51 (29).
3. U.S. EPA. 1980. Interim methods for the sampling and analysis of priority pollutants in sediments and fish tissue. October 1980. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.
4. Bellar, T., J. Lichtenburg, and S. Lonnesman. 1980. Recovery of organic compounds from environmentally contaminated bottom materials. In Contaminants and sediments, Volume 2, ed. R. Baker, Ann Arbor Science Publ., Inc., Ann Arbor, Michigan.
5. Rodriguez, C., W. McMahon, and K. Thomas. 1980. Method development for determination of polychlorinated hydrocarbons in municipal sludge. EPA Report-600/2-80-029.
6. U.S. EPA. Method 617. Organochlorine pesticides and PCB's. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

## METHOD 8090

### NITROAROMATICS AND CYCLIC KETONES

#### 1.0 Scope and Application

1.1 Method 8090 is used to determine the concentration of certain nitroaromatic and cyclic ketone compounds in groundwater, liquid, and solid sample matrices. Specifically Method 8090 may be used to detect the following substances:

Nitrobenzene  
Dinitrobenzene  
2,4-Dinitrotoluene  
2,6-Dinitrotoluene  
Isophorone  
Naphthoquinone

1.2 Method 8090 is recommended for use only by, or under the close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8090 provides cleanup and gas chromatographic conditions for the detection of ppb levels of nitroaromatic and cyclic ketone compounds. Prior to use of this method, the sample must be extracted using appropriate extraction techniques. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a flame ionization detector (FID). An aliquot of each sample will be spiked with standards to determine percent recovery and the limits of detection for that sample.

2.2 The sensitivity of Method 8090 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection for some of the compounds that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

#### 3.0 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 these materials must therefore 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 waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

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 min. Some high boiling materials, such as PCB's, 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 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. Plastics in particular must be avoided 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.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.6 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

TABLE 1. GAS CHROMATOGRAPHY OF NITROAROMATICS AND ISOPHORONE

Compound	Retention time (min)		Detection limit ( $\mu\text{g/l}$ )	
	Col. 1 <sup>a</sup>	Col. 2 <sup>b</sup>	ECD	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	-

<sup>a</sup>Gas-Chrom Q 80/100 mesh coated with 1.95% OF-1/1.5% OV-17 packed in a 4' x 1/4" O.D. glass column. FID analysis for IP and NB requires nitrogen carrier gas at 44 ml/min and 85° C column temperature. ECD analysis for the DNT's requires 10% methane/90% argon carrier gas at 44 ml/min flow rate and 145° C column temperature.

<sup>b</sup>Gas-Chrom Q 80/100 mesh coated with 3% OV-101 packed in a 10' x 1/4" O.D. glass column. FID analysis of IP and NB requires nitrogen carrier gas at 44 ml/min flow rate and 100° C column temperature. ECD analysis for the DNT's requires 10% methane/90% argon carrier gas at 44 ml/min flow rate and 150° C column temperature.

#### 4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

#### 4.2 Kuderna-Danish (K-D) apparatus

4.2.1 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.

4.2.2 Evaporative flask: 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012).

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Boiling chips: Solvent extracted, approximately 10/40 mesh.

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4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ \text{C}$ ). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture or flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatography column: 400-mm long x 10-mm I.D., with coarse-fritted plate on bottom and Teflon stopcock.

#### 5.0 Reagents

5.1 Sodium hydroxide: (ACS) 10 N in distilled water.

5.2 Sulfuric acid (1+1): (ACS) Mix equal volumes of conc.  $\text{H}_2\text{SO}_4$  with distilled water.

5.3 Methylene chloride: Pesticide quality or equivalent.

5.4 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at  $400^\circ \text{C}$  for 4 hr in a shallow tray).

5.5 Stock standards: Prepare stock standard solutions at a concentration of  $1.00 \mu\text{g}/\mu\text{l}$  by dissolving 0.100 g 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.

5.6 Acetone, hexane, methanol, toluene: Pesticide quality or equivalent.

5.7 Florisil: PR grade (60/100 mesh); purchase-activated at  $1250^\circ \text{F}$  and store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at  $130^\circ \text{C}$  in glass containers loosely covered with foil.

#### 6.0 Sample Collection, Preservation, and Handling

6.1 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.

6.2 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 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hr of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

7.1 Extraction. Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. An aliquot of each sample should be spiked with standards to determine the percent recovery and the limit of detection for that sample.

7.2 Cleanup and separation. If interferences prevent measurement of these compounds by GC, the following column cleanup procedure can be used to remove the interferences.

7.2.1 Prepare a slurry of 10 g of activated Florisil in 10% methylene chloride in hexane (v/v). Use it to pack a 10-mm I.D. chromatography column, gently tapping the column to settle the Florisil. Add 1 cm anhydrous sodium sulfate to the top of the Florisil.

7.2.2 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.

7.2.3 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/min. Discard the eluate from this fraction.

7.2.4 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.

7.2.5 Concentrate the collected fraction by the following K-D technique.

7.2.5.1 Add 1 or 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 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

7.2.5.2 When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min 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.

7.2.5.3 Add 1.0 ml toluene to the concentrator tube, and a clean boiling chip. Attach a two-ball micro-Snyder column. Prewet the Snyder column by adding about 0.5 ml of methylene chloride to the top. Place this KD 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 the water temperature as required to complete the concentration in 5-10 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood.

7.2.5.4 When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of toluene.

7.2.5.5 Adjust the final volume to 1.0 ml, stopper the concentrator tube, and store refrigerated if further processing will not be performed immediately.

7.3 The recommended gas chromatographic columns and operating conditions are:

Column 1: Gas-Chrom Q, 80/100 mesh, coated with 1.95% OF-1/1.5% OV-17 packed in a 4' x 1/4" O.D. glass column. FID analysis requires nitrogen gas at 44 ml/minute and 85° C column temperature. EDC analysis requires 10% methane/90% argon carrier gas at 44 ml/minute flow rate and 145° C column temperature.

Column 2: Gas-Chrom Q, 80/100 mesh, coated with 3% OV-101 packed in a 10' x 1/4" O.D. glass column. FID analysis requires nitrogen carrier gas at 44 ml/minute flow rate and 100° C column temperature. ECD analysis requires 10% methane/ 90% argon carrier gas at 44 ml/minute flow rate and 150° C column temperature.

## 7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.3. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1  $\mu\text{g}$  for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

### 7.4.2 External standard calibration procedure

7.4.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Using injections of 2 to 5  $\mu\text{l}$  of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.4.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.4.3.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{iS}$  = Concentration of the internal standard in  $\mu$ g/l.

$C_S$  = Concentration of the parameter to be measured in  $\mu$ g/l.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.4.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

## 7.5 Gas chromatographic analysis

7.5.1 Dinitrotoluenes can be analyzed on a gas chromatograph equipped with an electron capture detector. The other compounds covered by Method 8090 are to be analyzed on a gas chromatograph equipped with a flame ionization detector. Chromatography conditions are given in

Section 7.3. Table 1 summarizes estimated retention times and sensitivities that should be achieved by this method for clean water samples. Detection limits for a typical waste sample would be significantly higher.

7.5.2 Inject 2 to 5  $\mu\text{l}$  of the sample extract using the solvent flush technique. Smaller (1.0  $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.5.3 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

7.5.4 If peak detection is prevented by the presence of interferences, further cleanup is required. 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.

7.5.5 An example of a GC/FID chromatogram for nitrobenzene and isophorone is shown in Figure 1. Figure 2 shows a GC/ECD chromatogram of the dinitrotoluene.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were

obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
2,4-Dinitrotoluene	63	3.1	5-100	21	4
2,6-Dinitrotoluene	66	3.2	5-50	24	4
Isophorone	73	4.6	50-60	21	4
Nitrobenzene	71	5.9	90-100	24	4

#### 9.0 References

1. Development and application of test procedures for specific organic toxic substances in wastewaters. Category 4 - nitroaromatics and isophorone. Report for EPA Contract 68-03-2624 (in preparation).

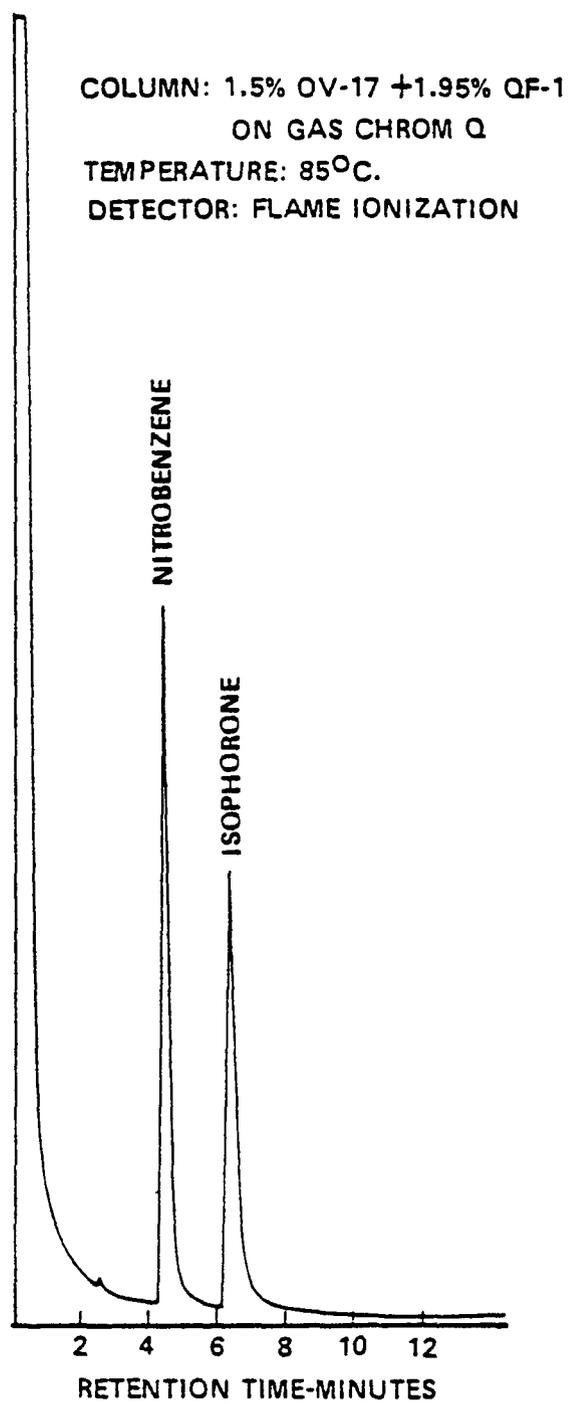


Figure 1. Gas chromatogram of nitrobenzene and isophorone.

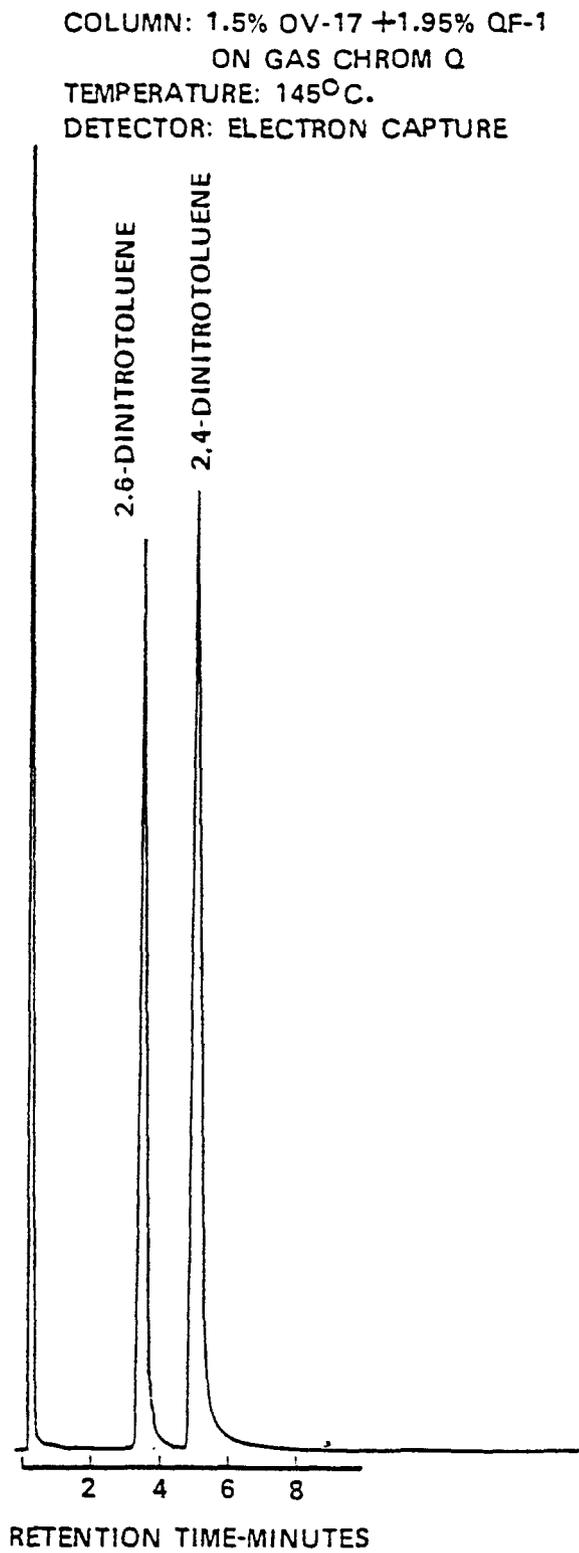


Figure 2. Gas chromatogram of dinitrotoluenes.

## METHOD 8100

### POLYNUCLEAR AROMATIC HYDROCARBONS

#### 1.0 Scope and Application

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in liquid and solid sample matrices. Specifically, Method 8100 may be used to detect the following substances:

Acenaphthene	Dibenz(a,h)anthracene
Acenaphthalene	7H-Dibenzo(c,g)carbazole
Anthracene	Dibenzo(a,e)pyrene
Benzo(a)anthracene	Dibenzo(a,h)pyrene
Benzo(a)pyrene	Dibenzo(a,i)pyrene
Benzo(b)fluoranthene	Fluoranthene
Benzo(ghi)perylene	Fluorene
Benzo(j)fluoranthene	Indeno(1,2,3-cd)pyrene
Benzo(k)fluoranthene	3-Methylcholanthrene
Chrysene	Naphthalene
Dibenzo(a,h)anthracene	Phenanthrene
Dibenz(a,h)acridine	Pyrene
Dibenz(a,j)acridine	

1.2 The packed-column gas chromatographic method described here 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. The use of capillary columns instead of packed columns, as described in this method, may adequately resolve these PAH. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, a liquid chromatographic approach (Method 8310) should be used for these compounds. The liquid chromatographic method will resolve all PAH compounds listed above.

1.3 Method 8100 is recommended for use only by, or under close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8100 provides cleanup and gas chromatographic conditions for detecting ppb levels of certain polynuclear aromatic hydrocarbons. Prior to analysis, samples must be extracted using appropriate techniques. Water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a neutral pH with methylene

chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID). An aliquot of each sample must be spiked with standards to determine the spike recovery and the limits of detection.

2.2 The sensitivity of Method 8100 usually depends on the level of interferences rather than on instrumental limitations.

### 3.0 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 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 cleanup technique is provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.4 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1  $\mu$ g/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower.

TABLE 1. GAS CHROMATOGRAPHY OF PAH

Compound <sup>a</sup>	Retention time (min)
Naphthalene	4.5
Acenaphthylene	10.4
Acenaphthene	10.8
Fluorene	12.6
Phenanthrene	15.9
Anthracene	15.9
Fluoranthene	19.8
Pyrene	20.6
Benzo(a)anthracene	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

<sup>a</sup>GC conditions: Chromosorb W-AW-DCMs 100/120 mesh coated with 3% OV-17, packed in a 6-ft x 2-mm I.D. glass column, with nitrogen carrier gas at 40 ml/min flow rate. Column temperature was held at 100° C for 4 min, then programmed at 8°/min to a final hold at 280° C.

#### 4.0 Apparatus and Materials

4.1 Drying column: 20-mm-I.D. pyrex chromatographic column with coarse frit.

#### 4.2 Kuderna-Danish (K-D) apparatus

4.2.1 Concentrator tube: 10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground-glass stopper (Size 22 joint) is used to prevent evaporation of extracts.

4.2.2 Evaporative flask: 500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012).

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4.2.3 Snyder column: Three-ball macro (Kontes K-50300-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Boiling chips: Solvent extracted, approximately 10/40 mesh.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection or capillary 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.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection or capillary 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.

4.5 Chromatographic column: 250 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

## 5.0 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.  $\text{H}_2\text{SO}_4$  with distilled water.

5.1.3 Sodium thiosulfate: (ACS) Granular.

5.2 Methylene chloride, pentane, cyclohexane (pesticide quality or equivalent).

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at  $400^\circ$  C for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of  $1.00 \mu\text{g}/\mu\text{l}$  by dissolving 0.100 g 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.

5.5 Silica gel: 100/120 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr at 130° C in a foil-covered glass container.

## 6.0 Sample Collection, Preservation, and Handling

6.1 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.

6.2 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 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hr 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 ppm of free chlorine per liter.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

### 7.1 Extraction

7.1.1 Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510), or a continuous liquid-liquid extractor (Method 3520). Extract solid samples with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. An aliquot of each sample should be spiked with standards to determine the percent recovery and the limit of detection for the sample.

7.1.2 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 5-10 min. At the proper rate of distillation, the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 min 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.

7.2 Cleanup and separation. If interferences prevent measurement of these compounds by GC, the following column cleanup procedure can be used to remove the interferences.

7.2.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1- to 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 min. At the chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 min 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.

7.2.2 Prepare a slurry of 10 g activated silica gel in methylene chloride and place this in a 10-mm-I.D. 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.

7.2.3 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.

7.2.4 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.

7.2.5 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.

7.2.6 Concentrate the collected fraction to less than 10 ml by K-D techniques using pentane to rinse the walls of the glassware. Proceed with gas chromatographic analysis.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are:

Column 1: Chromosorb W-AW-DCMs 100/120 mesh coated with 3% OV-17, packed in a 6-ft x 2-mm I.D. glass column, with nitrogen carrier gas at 40 ml/min flow rate. Column temperature was held at 100° C for 4 min, then programmed at 8°/min to a final hold at 280° C.

Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column, with helium carrier gas at 20 cm/sec flow rate. Column temperature was held at 35° C for 2 min, then programmed at 10°/min to 265° C and held for 12 min.

Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column, with helium carrier gas at 60 cm/sec flow rate. Column temperature was held at 35° C for 2 min, then programmed at 10°/min to 265° C and held for 3 min.

#### 7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.3. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

##### 7.4.2 External standard calibration procedure

7.4.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared for that parameter.

7.4.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.4.3.2 Using injections of 2 to 5  $\mu$ l of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{IS}$  = Response for the internal standard.

$C_{is}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_s$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_s/A_{is}$  against RF.

7.4.3.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

## 7.5 Gas chromatographic analysis

7.5.1 Chlorinated hydrocarbons are to be analyzed on a gas chromatograph equipped with a flame ionization detector according to column conditions described in Section 7.2. Table 1 summarizes retention times for packed column analyses.

7.5.2 Inject 2-5  $\mu\text{l}$  of the sample extract using the solvent flush technique. Smaller (1.0- $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.5.3 If the peak areas exceed the linear range of the system, dilute the extract and reanalyze.

## 8.0 Quality Control

8.1 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. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 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 sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1  $\mu\text{g/g}$  of sample, then the sensitivity of the instrument should be

increased or the extract subjected to additional cleanup. The fortified samples should be carried through all stages of the sample preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

## 9.0 References

1. 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.)
2. Sauter, A.D., Betowski, L.D., Smith, T.R., Strickler, V.A., Beimer, R.G., Colby, B.N., and Wilkinson, J.E. 1981. Fused silica capillary column GC/MS for the analysis of priority pollutants. Journal of HRC&CC 4:366-384.

## METHOD 8120

### CHLORINATED HYDROCARBONS

#### 1.0 Scope and Application

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons in groundwater, liquid and solid sample matrices. Specifically, Method 8120 may be used to detect the following substances:

Dichlorobenzenes	Benzotrichloride
Dichloromethylbenzene	Pentachlorohexane
Trichlorobenzenes	Hexachloroethane
Tetrachlorobenzenes	Hexachlorocyclohexane
Hexachlorobenzene	Hexachlorocyclopentadiene
Hexachlorobutadiene	Hexabutadiene
Benzyl chloride	2-Chloronaphthalene

1.2 Method 8120 is recommended for use only by, or under the close supervision of, experienced residue analysts.

#### 2.0 Summary of Method

2.1 Method 8120 provides cleanup and gas chromatographic conditions for detecting ppb levels of certain chlorinated hydrocarbons. Samples must be subjected to extraction techniques prior to analysis. Groundwater and other aqueous samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by direct injection. Solid samples are extracted at a neutral pH with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. A 2- to 5- $\mu$ l aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD). An aliquot of each sample must be spiked with standards to determine the spike recovery and the limits of detection.

2.2 The sensitivity of Method 8120 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

#### 3.0 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 these materials must therefore 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 waste to waste. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities.

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 min. Some high boiling materials, such as PCB's, 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 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the samples or solvent extract under the conditions of the analysis. Plastics, in particular, must be avoided 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.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.6 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1 µg/g of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 (below) when analyzing groundwater samples.

TABLE 1. GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Column 1 <sup>a</sup>	Method Detection limit (µg/l)
1,3-dichlorobenzene	4.0	1.19
1,4-dichlorobenzene	4.3	1.34
Hexachloroethane	4.8	0.03
1,2-dichlorobenzene	5.3	1.14
Hexachlorobutadiene	11.6	0.34
1,2,4-trichlorobenzene	12.4	0.05
Hexachlorocyclopentadiene	*1.5	-
2-chloronaphthalene	*2.5	0.94
Hexachlorobenzene	*7.0	0.05

<sup>a</sup>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-I.D. 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.

#### 4.0 Apparatus and Materials

4.1 Drying column: 20-mm I.D. pyrex chromatographic column with coarse frit.

#### 4.2 Kuderna-Danish (K-D) apparatus

4.2.1 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.

4.2.2 Evaporative flask: 500 ml (Kontes -57001-0500 or equivalent). Attach to concentrator tube with springs (Kontes K-662750-0012).

4.2.3 Snyder column: Three-ball macro (Kontes K503000-0121 or equivalent).

4.2.4 Snyder column: Two-ball micro (Kontes K569001-0219 or equivalent).

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4.2.5 Boiling chips: Solvent-extracted, approximately 10/40 mesh.

4.3: Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ \text{C}$ ). The bath should be used in a hood.

4.4 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron-capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.5 Chromatography column: 300 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

## 5.0 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.  $\text{H}_2\text{SO}_4$  with distilled water.

5.2 Methylene chloride, hexane and petroleum ether (boiling range  $30\text{-}60^\circ \text{C}$ ): Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous (purified by heating at  $400^\circ \text{C}$  for 4 hr in a shallow tray).

5.4 Stock standards: Prepare stock standard solutions at a concentration of  $1.00 \mu\text{g}/\mu\text{l}$  by dissolving 0.100 g 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.

5.5 Florisil: PR grade (60/100 mesh); purchase activated at  $1250^\circ \text{F}$  and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at  $130^\circ \text{C}$  in foil-covered glass containers.

## 6.0 Sample Collection, Preservation, and Handling

6.1 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.

6.2 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 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hr of collection, the sample should be adjusted to a pH range of 6.0-8.0 with sodium hydroxide or sulfuric acid.

6.3 All samples should be extracted immediately and must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedures

### 7.1 Extraction

7.1.1 Extract water samples at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3510). Extract solid samples with methylene chloride using either the Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures. Spiked samples are used to verify the applicability of the chosen extraction technique for each new sample type. An aliquot of each sample should be spiked with standards to determine the percent recovery and the limits of detection for that sample.

7.1.2 To avoid significant losses of volatile dichlorobenzenes during concentration, a constant gentle evaporation rate must be maintained, and the liquid volume must not be allowed to fall below 1-2 ml before removing the K-D from the hot water bath.

7.2 Cleanup and separation. If interferences prevent measurement of the compounds listed in Section 1.1 by GC, the following column cleanup procedure can be used to remove the interferences.

7.2.1 Adjust the sample extract to 10 ml.

7.2.2 Place a 12-g charge of activated Florisil (see 6.3) in a 10-mm I.D. chromatography column. After settling the Florisil by tapping the column, add a 1- to 2-cm layer of anhydrous granular sodium sulfate to the top.

7.2.3 Preelute 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 the chlorinated hydrocarbons.

7.2.4 Concentrate the fraction by K-D, prewetting 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.

7.3 Gas chromatography conditions. The recommended gas chromatographic column and operating conditions for the instrument are:

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-I.D. glass column with 5% methane/95% argon carrier gas at 30 ml/min flow rate. Column temperature is 75° C for low molecular weight compounds and 160° C for high molecular compounds.

#### 7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.3. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1 µg for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

##### 7.4.2 External standard calibration procedure

7.4.2.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with isooctane. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Using injections of 2 to 5 µl of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to

If the samples will not be extracted within 48 hr of collection, the sample should be adjusted to a pH range of 6.0 to 8.0 with sodium hydroxide or sulfuric acid. Prior to addition of acid or base, mark the water meniscus on the side of the sample bottle for later determination of sample volume.

6.3 All samples must be extracted within 7 days and completely analyzed within 14 days of collection.

## 7.0 Procedures

### 7.1 Sample preparation

7.1.1 Water samples should be extracted at a neutral pH with methylene chloride as a solvent, using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Soxhlet extraction (Method 3540) or sonication procedures (Method 3550) are used for solid samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type.

7.2 The recommended gas chromatographic column and operating conditions for the instrument are:

Column 1a Conditions: Supelcoport (100/120 mesh) coated with 5% SP-2401 packed in a 180-cm long x 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature, programmed: initial 150° C, hold for 1 min, then program at 25° C/min to 220° C and hold.

Column 1b Conditions: Same as Column 1a, except nitrogen carrier gas at a flow rate of 30 ml/min. Temperature, programmed: initial 170° C, hold 2 min, then program at 20° C/min to 220° C and hold.

Column 2 Conditions: Supelcoport (100/120 mesh) coated with 3% SP-2401 packed in a 180-cm long x 2-mm I.D. glass column with helium carrier gas at a flow rate of 25 ml/min. Column temperature, programmed, initial 170° C, hold for 7 min, then program at 10° C/min to 250° C and hold.

Column 3 Conditions: Gas Chrom Q (100/120 mesh) coated with 15% SE-54 packed in a 50-cm long x 1/8 in. O.D. Teflon column with nitrogen carrier gas at a flow rate of 30 ml/min. Temperature, programmed: initial 100° C, then program immediately at 25° C/min to 200° C and hold.

### 7.3 Calibration

Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.2. By injecting secondary standards, adjust the

sensitivity of the analytical system for each compound being analyzed so as to detect quantities of less than or equal to 1  $\mu\text{g}$  for waste samples. Detection limits to be used for groundwater analysis are given in Table 1. Calibrate the chromatographic system using either the external standard technique (Section 7.4.2) or the internal standard technique (Section 7.4.3).

### 7.3.1 External standard calibration procedure

7.3.1.1 For each parameter of interest, prepare calibration standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with hexane or other suitable solvent. One of the external standards would be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.1.2 Using injections of 2 to 5  $\mu\text{l}$  of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.1.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.2 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.2.1 Prepare calibration standards at a minimum of three concentration levels for each parameter of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount

of one or more internal standards, and dilute to volume with hexane or other suitable solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.2.2 Using injections of 2 to 5  $\mu\text{l}$  of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$\text{RF} = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{iS}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_S$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{iS}$  against RF.

7.3.2.3 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.

## 7.4 Analysis

7.4.1 Inject 2 to 5  $\mu\text{l}$  of the sample extract using the solvent-flush technique. Smaller (1.0- $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.4.2 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. 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.

7.4.4 It should be noted that Naled can be completely converted to Dichlorvos on the GC column.

7.4.5 Examples of chromatograms for organophosphorus pesticides are shown in Figures 1 through 4.

## 8.0 Quality Control

8.1 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.

8.2 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 waste samples of waste should be analyzed to validate the accuracy of the analysis. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry should be used (Section 8.3).

### 8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to exceed 3 sec per scan utilizing 70-V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all-glass or glass-lined materials is recommended. A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program should be interfaced to the mass spectrometer.

8.3.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices, such as those described for Method 8250.

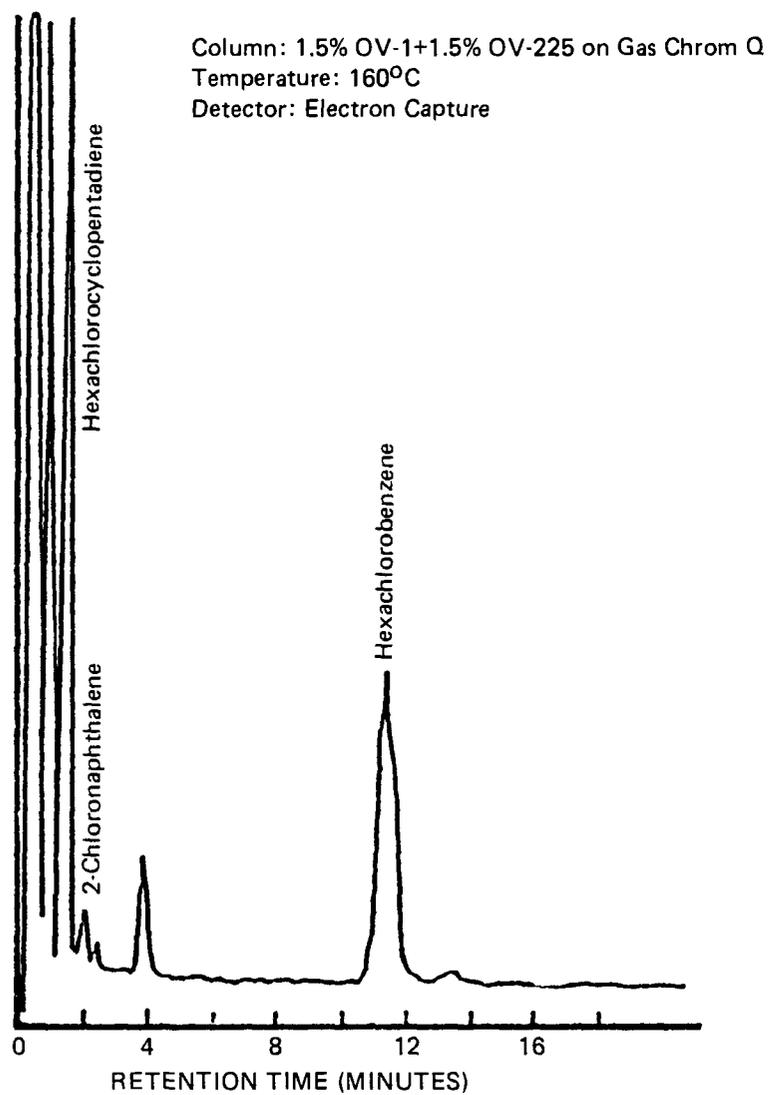


Figure 2. Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).

2. Mills, P.A. 1968. Variation of Florisil activity: Simple method for measuring absorbent capacity and its use in standardizing Florisil columns. J. Assoc. Official Analyt. Chem. 51(29).

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation (%)	Spike range ( $\mu\text{g/l}$ )	Number of analyses	Matrix types
2-Chloronaphthalene	76	25	19.1-268	18	3
1,2-Dichlorobenzene	82	10	29.8-356	18	3
1,3-Dichlorobenzene	86	18	20.4-238	18	3
1,4-Dichlorobenzene	89	20	23.0-324	18	3
Hexachlorobenzene	95	12	1.29-14.9	18	3
Hexachlorobutadiene	96	10	3.12-36.8	18	3
Hexachloroethane	99	12	1.02-14.8	18	3
1,2,4-Trichlorobenzene	96	16	15.1-216	18	3

## METHOD 8140

### ORGANOPHOSPHORUS PESTICIDES

#### 1.0 Scope and Application

1.1 Method 8140 is a gas chromatographic (GC) method for determining pesticides in groundwater and waste samples. Specifically, Method 8140 may be used to determine the following parameters:

Azinphos methyl	Merphos
Bolstar (Sulprofos)	Mevinphos
Chlorpyrifos	Monochrotophos
Coumaphos	Naled
Demeton	Parathion methyl
Diazinon	Parathion
Dichlorvos	Phorate
Dimethoate	Ronnel
Disulfoton	Stirophos (Tetrachlorvinphos)
EPN	Sulfotepp
Ethoprop	TEPP
Fensulfothion	Tokuthion (Prothiofos)
Fenthion	Trichloronate
Malathion	

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative technique if mass spectroscopy is not employed. Section 8.3 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 The estimated detection limits for each of the parameters in wastewater are listed in Table 1. The detection limit for a specific waste sample may differ from those listed, depending upon the nature of interferences and the sample matrix.

1.4 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms.

#### 2.0 Summary of Method

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to the use of this method, appropriate sample extraction techniques must be used. Water samples are extracted at a neutral pH with methylene chloride as a solvent using a separatory funnel (Method 3510) or a continuous liquid-liquid extractor (Method 3520). Both neat and diluted organic liquids may be analyzed by

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND ESTIMATED DETECTION LIMITS FOR METHOD 8140 IN WASTEWATER<sup>a</sup>

Parameter	GC column <sup>b</sup>	Retention time (min)	Estimated detection limit (µg/l)
Demeton-S	1a	1.16	0.25
Phorate	1a	1.43	0.15
Disulfoton	1a	2.10	0.20
Demeton-O	1a	2.53	0.25
Trichloronate	1a	2.94	0.15
Fenthion	1a	3.12	0.10
Tokuthion	1a	3.40	0.5
Bolstar	1a	4.23	0.15
Fensulfothion	1a	6.41	1.5
Azinphos methyl	1a	6.80	1.5
Coumaphos	1a	11.6	1.5
Dichlorvos	1b,3	0.8, 1.50	0.1
Mevinphos	1b	2.41, 5.51	0.3
Stirophos	1b,3	8.52	5.0
Ethoprop	2	3.02	0.25
Parathion methyl	2	3.37	0.3
Ronnel	2	5.57	0.3
Chlorpyrifos	2	6.16	0.3
Merphos	2	7.45	0.25
Diazinon	2	7.73	0.6
Naled	3	3.28	0.1

<sup>a</sup>Information taken from Reference 1.

<sup>b</sup>Column conditions are as follows:

Column 1a Conditions: Supelcoport (100/120 mesh) coated with 5% SP-2401 packed in a 180-cm long x 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature, programmed: initial 150° C, hold for 1 min, then program at 25° C/min to 220° C and hold.

Column 1b Conditions: Same as Column 1a, except nitrogen carrier gas at a flow rate of 30 ml/min. Temperature, programmed: initial 170° C, hold 2 min, then program at 20° C/min to 220° C and hold.

Column 2 Conditions: Supelcoport (100/120 mesh) coated with 3% SP-2401 packed in a 180-cm long x 2-mm I.D. glass column with helium carrier gas at a flow rate of 25 ml/min. Column temperature, programmed, initial 170° C, hold for 7 min, then program at 10° C/min to 250° C and hold.

Column 3 Conditions: Gas Chrom Q (100/120 mesh) coated with 15% SE-54 packed in a 50-cm long x 1/8 in. O.D. Teflon column with nitrogen carrier gas at a flow rate of 30 ml/min. Temperature, programmed: initial 100° C, then program immediately at 25° C/min to 200° C and hold.

direct injection. Soxhlet extraction (Method 3540) or sonication (Method 3550) procedures are used for solid samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. A gas chromatograph with a flame photometric or thermionic detector is used for analysis.

2.2 Each sample must be spiked with an appropriate standard to determine the percent recovery and the detection limit for that sample.

### 3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400° C for 15 to 30 min. Some thermally stable materials such as PCB's may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled. Unique samples may require special cleanup approaches to achieve the estimated detection of limits listed in Table 1. The use of florisil and silica gel as cleanup materials for the compounds in this method has been demonstrated to yield recoveries less than 85% and is not recommended for use in this method (1). Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution

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profile and demonstrate that the recovery of each compound of interest is no less than 85%.

3.3 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus. Elemental sulfur, however, may interfere with the determination of certain organophosphorus pesticides by flame photometric gas chromatography.

3.4 A halogen-specific detector (electrolytic conductivity or micro-coulometric) is very selective for the halogen-containing pesticides and is recommended for use with dichlorvos, naled and stirophos.

3.5 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

3.6 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1  $\mu\text{g/g}$  of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 when analyzing groundwater samples.

### 4.0 Apparatus and Materials

#### 4.1 Glassware.

4.1.1 Drying column: Chromatographic column 400-mm long x 19-mm I.D. with coarse frit.

4.1.2 Chromatographic column: 300-mm long x 10-mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

4.1.3 Concentrator tube, Kuderna-Danish: 10-ml, graduated. Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

4.1.4 Evaporative flask, Kuderna-Danish: 500-ml. Attach to concentrator, tube with springs.

4.1.5 Snyder column, Kuderna-Danish: three-ball macro.

4.1.6 Vials: Amber glass, 10- to 15-ml capacity with Teflon-lined screw-cap.

4.2 Boiling chips: Approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.4 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.5 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

#### 4.5.1 Columns:

Column 1: 180-cm long x 2-mm I.D. glass, packed with 5% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

Column 2: 180-cm long x 2-mm I.D. glass, packed with 3% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

Column 3: 50-cm long x 1/8 inch O.D. Teflon, packed with 15% SE-54 on Gas Chrom Q (80/100 mesh).

4.5.2 Detector: These detectors have proven effective in analysis for the parameters listed in Section 1.1 and were used to develop the accuracy and precision statements in Section 8.4.

Phosphorus-specific: Nitrogen/Phosphorus (N/P), operated in phosphorus-sensitive mode, or Flame Photometric (FPD). The FPD is more selective for phosphorus than the N/P.

Halogen-specific: Electrolytic Conductivity or Microcoulometric. These are very selective for those pesticides containing halogen substituents.

## 5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.2 Hexane, methylene chloride: Pesticide quality or equivalent.

5.3 Sodium sulfate: (ACS) Granular, anhydrous. Purify by heating at 400° C for 4 hr in a shallow tray.

5.4 Stock standard solutions (1.00 µg/µl): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.4.1 Prepare stock standard solutions by accurately weighing about 0.0500 g of pure material. Dissolve the material in pesticide-quality iso-octane or other suitable solvent and dilute to volume in a 10-ml volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source. (Disulfoton standards should be prepared on a monthly basis.)

5.4.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

## 6.0 Sample Collection, Preservation, and Handling

6.1 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 groundwater 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.

6.2 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 hr will elapse before delivery to the laboratory.

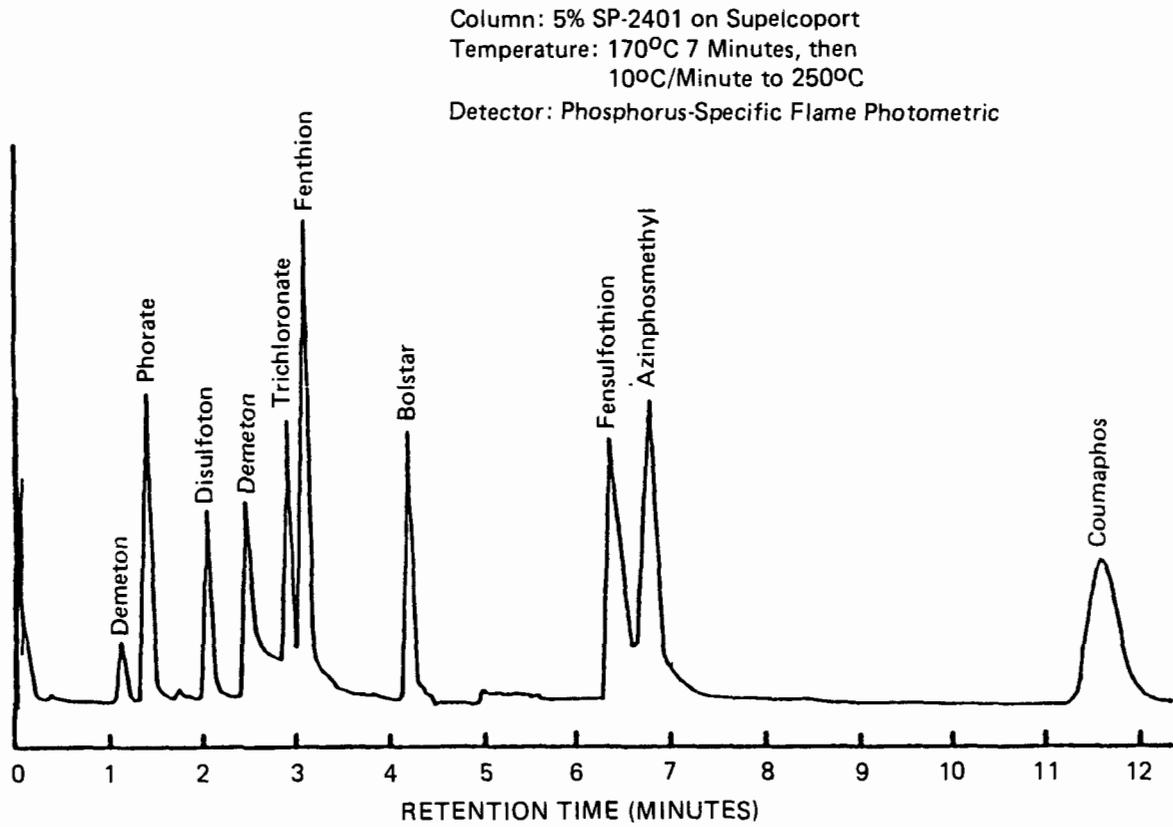


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

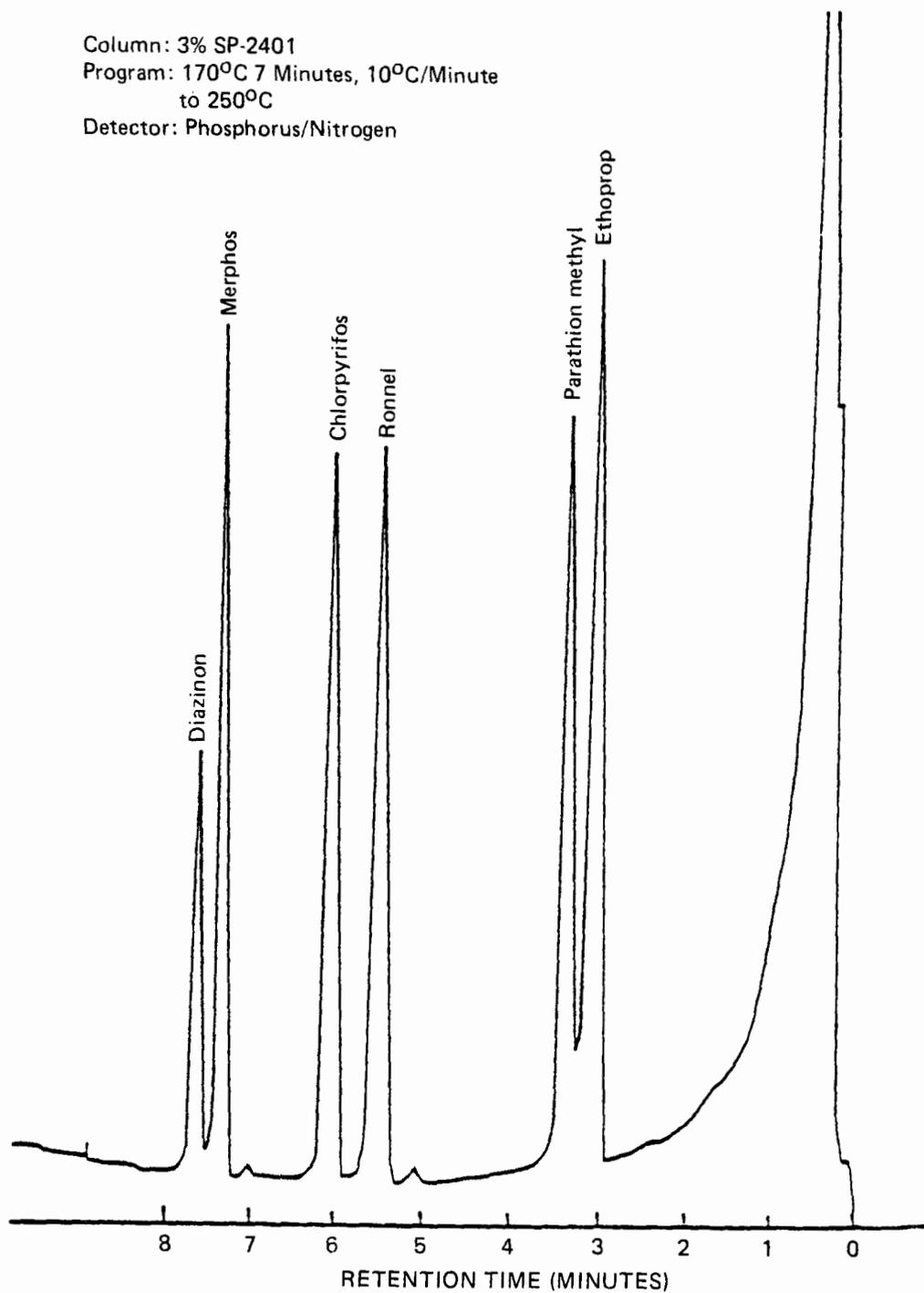


Figure 2. Gas chromatogram of organophosphorus pesticides (Example 2).

Column: 15% SE-54 on Gas Chrom Q  
Temperature: 100°C Initial, then  
25°C/Minute to 200°C  
Detector: Hall Electrolytic Conductivity—Oxidative Mode

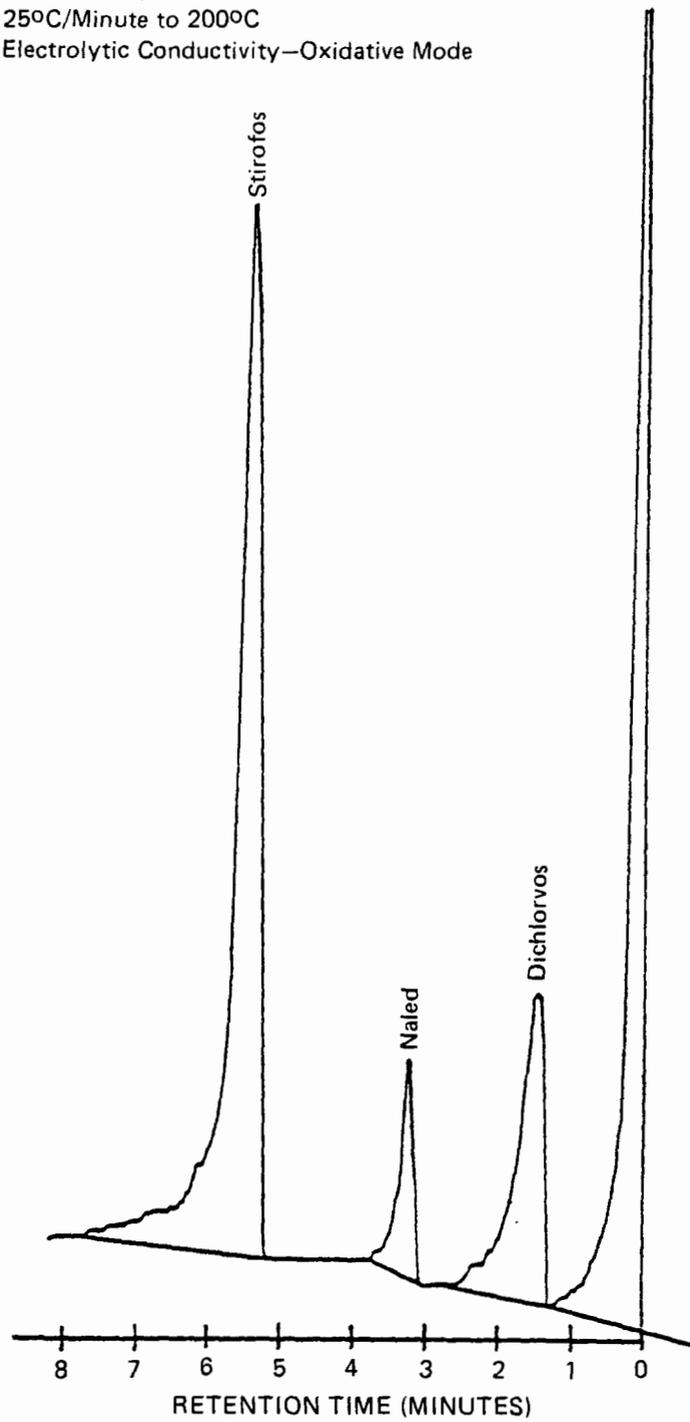


Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

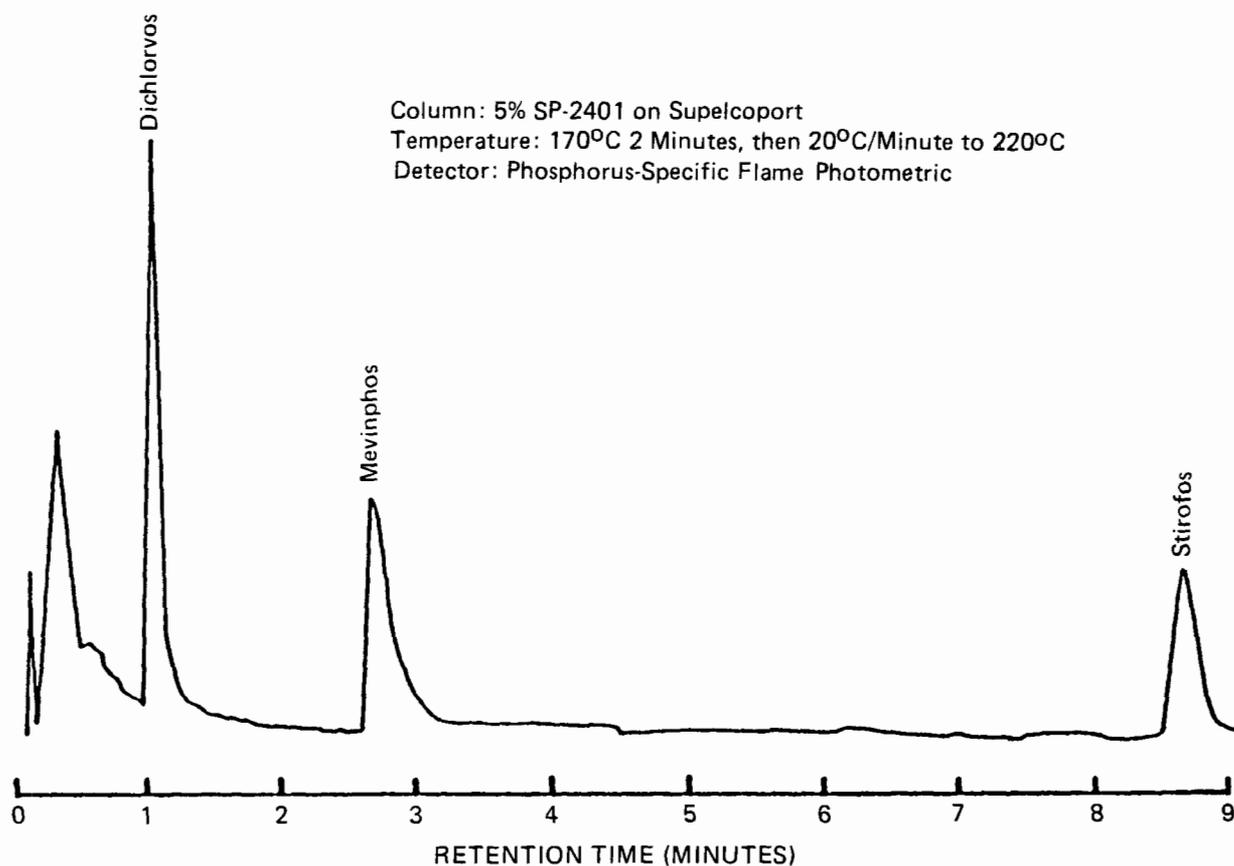


Figure 4. Gas chromatogram of organophosphorus pesticides (Example 4).

8.3.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP (decafluorotriphenyl phosphine) performance criteria are achieved, as described in Method 8250.

8.3.4 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 nanograms of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

1. The molecular ion and all other ions present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to  $\pm 10\%$ . For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20-40%.

2. The retention time of the compound in the sample must be within 6 sec of the retention time for the same compound in the standard solution.

3. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.5 Where available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.3.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

#### 8.4 Method performance

8.4.1 Estimated detection limits (EDL) and associated chromatographic conditions for wastewater are listed above in Table 1. The detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise.

8.4.2 Single operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION FOR METHOD 8140<sup>a</sup>

Parameter	Average percent recovery	Standard deviation (%)	Spike range (µg/l)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

<sup>a</sup>Information taken from Reference 3.

## 9.0 References

1. Development of analytical test procedures for organic pollutants in wastewater; Report for EPA Contract No. 68-03-2711. (In preparation)
2. Burke, J.A. 1965. Gas chromatography for pesticide residue analysis; some practical aspects. Journal of the Association of Official Analytical Chemists 48:1037.
3. Pesticide methods evaluation. Letter Reports #6, 12A, and 14 in EPA Contract No. 68-03-2697.

## METHOD 8150

### CHLORINATED HERBICIDES

#### 1.0 Scope and Application

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides in groundwater and waste samples. Specifically, Method 8150 may be used to determine the following compounds:

- 2,4-D
- 2,4-DB
- 2,4,5-T
- 2,4,5-TP
- Dalapon
- Dicamba
- Dichloroprop
- Dinoseb
- MCPA
- MCPP

Since these compounds are produced and used in various forms (i.e., acid, salt, ester, etc.), the method includes a hydrolysis step to convert the herbicide to the acid form prior to analysis.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.3 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (explosive, carcinogenic).

#### 2.0 Summary of Method

Method 8150 provides extraction, esterification and gas chromatographic conditions for the analysis of chlorinated acid herbicides in water and waste samples. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography

employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (2). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations. Table 1 lists the limits of detection that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR METHOD 8150 IN WASTEWATER

Parameter	Retention time (min) <sup>a</sup>				Estimated detection limit (µg/l)
	Col. 1a	Col. 1b	Column 2	Column 3	
Dicamba	1.2	--	1.0	--	1.0
2,4-D	2.0	--	1.6	--	1.0
2,4,5-TP	2.7	--	2.0	--	0.1
2,4,5-T	3.4	--	2.4	--	0.1
2,4-DB	4.1	--	--	--	1.0
Dalapon	--	--	--	5.0	1.0
MCPP	--	3.4	--	--	200
MCPA	--	4.1	--	--	200
Dichloroprop	--	4.8	--	--	1.0
Dinoseb	--	11.2	--	--	0.1

<sup>a</sup>Column conditions are as follows:

Column 1a conditions: 95% Argon/5% Methane carrier gas as a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° C to 150° C at 10°/min.

### 3.0 Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing hardware that lead to discrete artifacts or elevated baselines in gas chromatograms. All these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.1.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water and rinses with tap and distilled water. The glassware should then be drained dry and heated in a muffle furnace at 400° C for 15 to 30 min. Some thermally stable materials such as PCB's may not be eliminated by this treatment. Solvent rinses with acetone and pesticide quality hexane may be substituted for the muffle furnace heating. Volumetric ware should not be heated in a muffle furnace. After drying and cooling, glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from waste to waste, depending upon the nature and diversity of the waste being sampled.

3.3 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction of the basic solution removes many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

3.6 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. Standard quality assurance practices should be used with this method. Field replicates should be

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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 analyses. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used. Detection limits for groundwater and EP extracts are given in Table 1. Detection limits for these compounds in wastes should be set at 1 µg/g.

#### 4.0 Apparatus and Materials

4.1 Glassware (all specifications are suggested. Catalog numbers are included for illustration only).

4.1.1 Separatory funnel: 2000-ml, with Teflon stopcock.

4.1.2 Drying column: Chromatographic column 400 mm long x 19 mm I.D. with coarse frit.

4.1.3 Chromatographic column: 300 mm long x 10 mm I.D. with coarse fritted disc at bottom and Teflon stopcock.

4.1.4 Concentrator tube, Kuderna-Danish: 10-ml, graduated. Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.1.5 Evaporative flask, Kuderna-Danish: 500-ml. Attach to concentrator tube with springs.

4.1.6 Snyder column, Kuderna-Danish: three-ball macro.

4.1.7 Snyder column, Kuderna-Danish: two-ball micro.

4.1.8 Vials: Amber glass, 10- to 15-ml capacity with Teflon-lined screw-cap.

4.1.9 Erlenmeyer flask: Pyrex, 250-ml with 24/40 ground-glass joint.

4.2 Boiling chips: approximately 10/40 mesh. Heat to 400° C for 30 min or Soxhlet extract with methylene chloride.

4.3 Diazald Kit: recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. No. 210,025-2).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control (+2° C). The bath should be used in a hood.

4.5 Glass wool: Acid washed.

4.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

4.7 Pipet: Pasteur, glass, disposable (140-mm x 5-mm I.D.).

4.8 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector and stripchart recorder. A data system is recommended for measuring peak areas.

4.8.1 Column 1: 180 cm long x 4 mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.8.2 Column 2: 180 cm long x 4 mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.8.3 Column 3: 180 cm long x 2 mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopak C or equivalent.

4.8.4 Detector: Electron capture. This detector has proven effective in the analysis of wastewaters for the parameters listed in Section 1.1. Guidelines for the use of alternate detectors are provided in Section 7.4.

4.9 Wrist Shaker: Burrel Model 75 or equivalent.

## 5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.2 Sodium hydroxide solution (10 N): Dissolve 40 g NaOH in reagent water and dilute to 100 ml.

5.3 Sulfuric acid solution (1:1): Slowly add 50 ml H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) to 50 ml of reagent water.

5.4 Sulfuric acid solution (1:3): Slowly add 1 part H<sub>2</sub>SO<sub>4</sub> (sp. gr. 1.84) to 3 parts reagent water.

5.5 Hydrochloric acid: (ACS) Mix 1 part of concentrated acid with 9 parts distilled water (v/v).

5.6 Potassium hydroxide solution: 37% aqueous solution (w/v). Prepare with reagent grade potassium hydroxide pellets and distilled water.

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5.7 Acetone, hexane, toluene, methanol: Pesticide quality or equivalent.

5.8 Diethyl ether: Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). 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.

5.9 Sodium sulfate: (ACS) Granular, acidified as follows: Slurry 100 g sodium sulfate with enough diethyl ether to just cover the solid, then add 0.1 ml of concentrated sulfuric acid. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and measure the pH of the mixture. It must be below pH 4. Store at 130° C. Several levels of purification may be required in order to reduce background phthalate levels to an acceptable level: (1) Heat 4 hr at 400° C in a shallow tray, (2) Heat 16 hr at 450-400° C in a shallow tray, (3) Soxhlet extract with methylene chloride for 48 hr.

5.10 Carbitol (diethylene glycol monoethyl ether).

5.11 N-methyl (-N-nitroso-p-toluenesulfonamide (DiazaId): High purity available from Aldrich Chemical Co.

5.12 5% acidified Na<sub>2</sub>SO<sub>4</sub>: Use 50 g of acidified anhydrous Na<sub>2</sub>SO<sub>4</sub> to every 1000 ml distilled H<sub>2</sub>O.

5.13 Stock standard solutions (1.00 µg/µl): Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.13.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide-quality diethyl ether and dilute to volume in a 10-ml volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.13.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4° C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.13.3 Stock standard solutions must be replaced after 1 week, or sooner if comparison with check standards indicates a problem.

5.14 Diazomethane solution: Follow generator kit instructions. Store in freezer in glass bottle stoppered with cork. Check for deterioration.

## 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of Tygon and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 7 days and completely analyzed within 30 days of extraction.

## 7.0 Procedures

### 7.1 Sample preparation

#### 7.1.1 Solid extraction

7.1.1.1 Thoroughly mix moist solids and weigh an amount of wet sample equivalent to 50 g of dry weight into 500-ml wide-mouth Erlenmeyer flasks.

7.1.1.2 Acidify solids with reagent grade concentrated hydrochloric acid using 2-3 ml to pH 2. Allow to stand for 15 min with occasional stirring until the pH remains below 2. Add more acid if necessary.

7.1.1.3 Add 20 ml of acetone to each flask containing the acidified sample and clamp the stopper in place. Mix the contents of the flasks for 20 min using the wrist-action shaker. Add 80 ml of redistilled ethyl ether to the same flasks and shake again for 20 min.

7.1.1.4 Decant the extracts into 2-liter separatory funnels containing 250 ml of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified

sodium sulfate equal to the weight of the sample may be added if necessary.

7.1.1.5 To ensure adequate recovery, measure the volume of extract into a graduated cylinder at each decanting step before adding the extract to the separatory funnel. If the recovered volume is not better than 75%, an additional extraction must be conducted.

7.1.1.6 Check the pH to ensure that it remains below 2. If the pH is not below 2, add more hydrochloric acid until stabilized. Add 20 ml of acetone to each Erlenmeyer flask containing the sediment and shake on the wrist-action shaker for 10 min. Again, add 80 ml of ethyl ether, shake for 10 min and decant extract into their respective separatory funnels. Repeat this step once more, collecting the acetone-ether extracts in the funnels containing the 5% acidified sodium sulfate solution.

7.1.1.7 Gently mix the content of each separatory funnel for about 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract (top layer) in a 500-ml ground-glass Erlenmeyer flask. Reextract the water layer with 25 ml of ethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the respective Erlenmeyer flasks.

7.1.1.8 Add 30 ml of distilled water to the extract in the Erlenmeyer flasks and refrigerate. Note: This is a good stopping point or, if time permits, continue to step 7.1.1.12.

7.1.1.9 Add 5 ml of 37% (w/w) aqueous potassium hydroxide and boiling chips to the extract in the flask and fit them with a one-ball Snyder column. Evaporate the ethyl ether on the steam bath and continue to heat for 90 min.

7.1.1.10 Remove the flasks from the steam bath, allow them to cool, and transfer the water solutions to 125-ml separatory funnels. Extract the basic solutions once with 40 ml and then twice with 20 ml of redistilled ethyl ether. Allow sufficient time for the layers to separate, and discard the ether layer each time. Note: This is a solvent cleanup step. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.1.11 Add 5 ml cold 25% (v/v) sulfuric acid to the contents of each funnel to adjust the pH to 2. Be sure to check the pH at this point. Extract the herbicides once with 40 ml and two more times with 20 ml of ethyl ether.

7.1.1.12 Collect the ether extracts in 125-ml Erlenmeyer flasks containing 1.0 g of acidified anhydrous  $\text{Na}_2\text{SO}_4$ . Stopper and allow the extracts to remain in contact with the acidified  $\text{Na}_2\text{SO}_4$ . Store the samples overnight in the refrigerator.  
Note: This is a good stopping point.

7.1.1.13 Concentrate extract and perform esterification, starting with step 7.2.2.7.

## 7.1.2 Liquid extraction

7.1.2.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel. Check the pH with wide-range pH paper and adjust to pH less than 2 with sulfuric acid (1:1).

7.1.2.2 Add 150 ml diethyl ether to the sample bottle, seal, and shake 30 sec to rinse the walls. Transfer the solvent into the separatory funnel. Extract the sample by shaking the funnel for 2 min with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between the 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. Drain the water phase into a 1-liter Erlenmeyer flask. Then collect the extract in a 250-ml ground-glass Erlenmeyer flask containing 2 ml of 37% aqueous potassium hydroxide. Approximately 80 ml of the diethyl ether will remain dissolved in the aqueous phase.

7.1.2.3 Extract the sample two more times using 50 ml of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.1.2.4 Add 1 or 2 clean boiling chips to the 250-ml flask, add 15 ml distilled water, and attach a three-ball Snyder column. Prewet the Snyder column by adding 1 ml diethyl ether to the top. Place the apparatus on a hot water bath ( $60^\circ$  to  $65^\circ$  C), such that the bottom of the flask is bathed in the water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.1.2.5 Transfer the solution to a 60-ml separatory funnel using 5 to 10 ml of distilled water. Wash the basic solution twice by shaking for 1 min with 20-ml portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.1.2.6 Acidify the contents of the separatory funnel to pH 2 by adding 2 ml of cold (4° C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 ml diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into the 250-ml Erlenmeyer, then pour the organic layer into a 125-ml Erlenmeyer containing about 0.5 g of acidified anhydrous sodium sulfate. Repeat the extraction twice more with 10-ml aliquots of diethyl ether, combining all solvent in the 125-ml flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.1.2.7 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-ml Kuderna-Danish flask equipped with a 10-ml concentrator tube. Use liberal washings of ether. Use a glass rod to crush any caked sodium sulfate during the transfer.

7.1.2.8 Add 1 to 2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml diethyl ether to the top. Place the K-D apparatus on a hot water bath (60° to 65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min while cooling.

7.1.2.9 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of diethyl ether. Final volume should be 4.0 ml. The sample is now ready for derivatization with diazomethane to form methyl esters.

### 7.1.3 Esterification

7.1.3.1 The diazomethane derivatization (1) procedure described below will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. Diazomethane is a carcinogen and can explode under certain conditions. The following precautions should be taken:

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90° C - EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers - EXPLOSION may result.
- Store away from alkali metals - EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.1.3.2 Instructions for preparing diazomethane are provided with the generator kit.

7.1.3.3 Add 2 ml of diazomethane solution and let sample stand for 10 min with occasional swirling.

7.1.3.4 Rinse inside wall of ampule with several hundred  $\mu$ l of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature).

7.1.3.5 Dissolve residue in 5 ml of hexane. Analyze by gas chromatography.

## 7.2 Gas chromatography conditions

7.2.1 The recommended gas chromatographic column materials and operating conditions for the instrument are:

<u>Parameter</u>	<u>Column</u>
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

Column 1a conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature isothermal at 185° C.

Column 1b temperature: 140° C for 6 min and then programmed to 200° C at 10°/min.

Column 2 conditions: 95% Argon/5% Methane carrier gas at a flow rate of 70 ml/min. Column temperature, isothermal at 185° C.

Column 3 conditions: UHP Nitrogen carrier gas at a flow rate of 25 ml/min. Column temperature programmed from 100° to 150° C at 10°/min.

7.2.2 The use of capillary (open-tubular) columns is acceptable if appropriate response and separation can be demonstrated.

### 7.3 Calibration

7.3.1 Establish gas chromatographic operating parameters equivalent to those indicated above in Table 1. The gas chromatographic system can be calibrated using the external standard technique (Section 7.3.2) or the internal standard technique (Section 7.3.3).

#### 7.3.2 External standard calibration procedure

7.3.2.1 For each parameter of interest, prepare working standards at a minimum of three concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with diethyl ether. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.3.2.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2. Using injections of 2 to 5  $\mu$ l of each esterified working standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each parameter. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), can be calculated for each parameter at each standard concentration. If the relative standard deviation of the calibration factor is less than 10% over the working range, linearity through the origin can be assumed and the average calibration factor can be used in place of a calibration curve.

7.3.2.3 The working calibration curve or calibration factor must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than +10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor may be prepared for that parameter.

7.3.3 Internal standard calibration procedure. To use this approach, the analyst must select one or more internal standards similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.3.1 Prepare working standards at a minimum of three concentration levels for each parameter of interest in the acid form by adding volumes of one or more stock standards to a volumetric flask, and dilute to volume with diethyl ether. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the detector.

7.3.3.2 Prepare calibration standards from the free acids by esterification of the working standards as described under Liquid Extraction, Section 7.1.2.

7.3.3.3 Prior to injection, add a known constant amount of one or more internal standards to each calibration standard.

7.3.3.4 Using injections of 2 to 5  $\mu\text{l}$  of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$\text{RF} = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{iS}$  = Response for the internal standard.

$C_{iS}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_S$  = Concentration of the parameter to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{IS}$  against RF.

- 7.3.3.5 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than  $\pm 10\%$ , the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared for that compound.
- 

7.3.4 Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

## 7.4 Analysis

7.4.1 Inject 2 to 5  $\mu\text{l}$  of the sample extract using the solvent-flush technique. Smaller (1.0- $\mu\text{l}$ ) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05  $\mu\text{l}$ , and the resulting peak size, in area units.

7.4.2 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.3 If peak detection is prevented by the presence of interferences, further cleanup is required. 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.

7.4.4 Examples of chromatograms for chlorophenoxy herbicides are shown in Figures 1 to 3.

## 8.0 Quality Control

8.1 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.

8.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)  
Temperature: Isothermal at 185°C  
Detector: Electron Capture

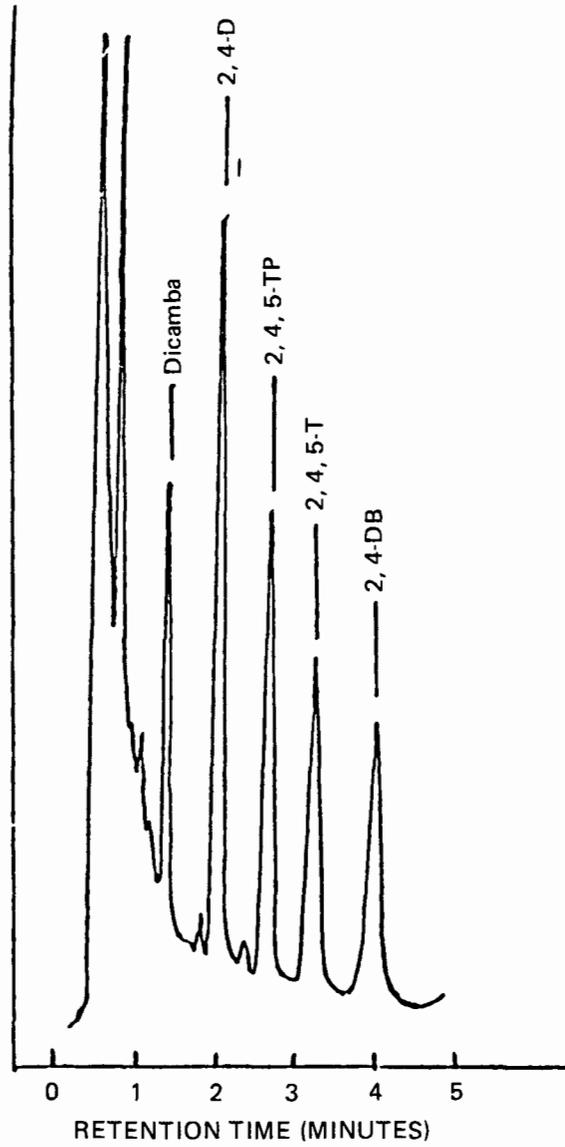


Figure 1. Gas chromatogram of chlorinated herbicides.

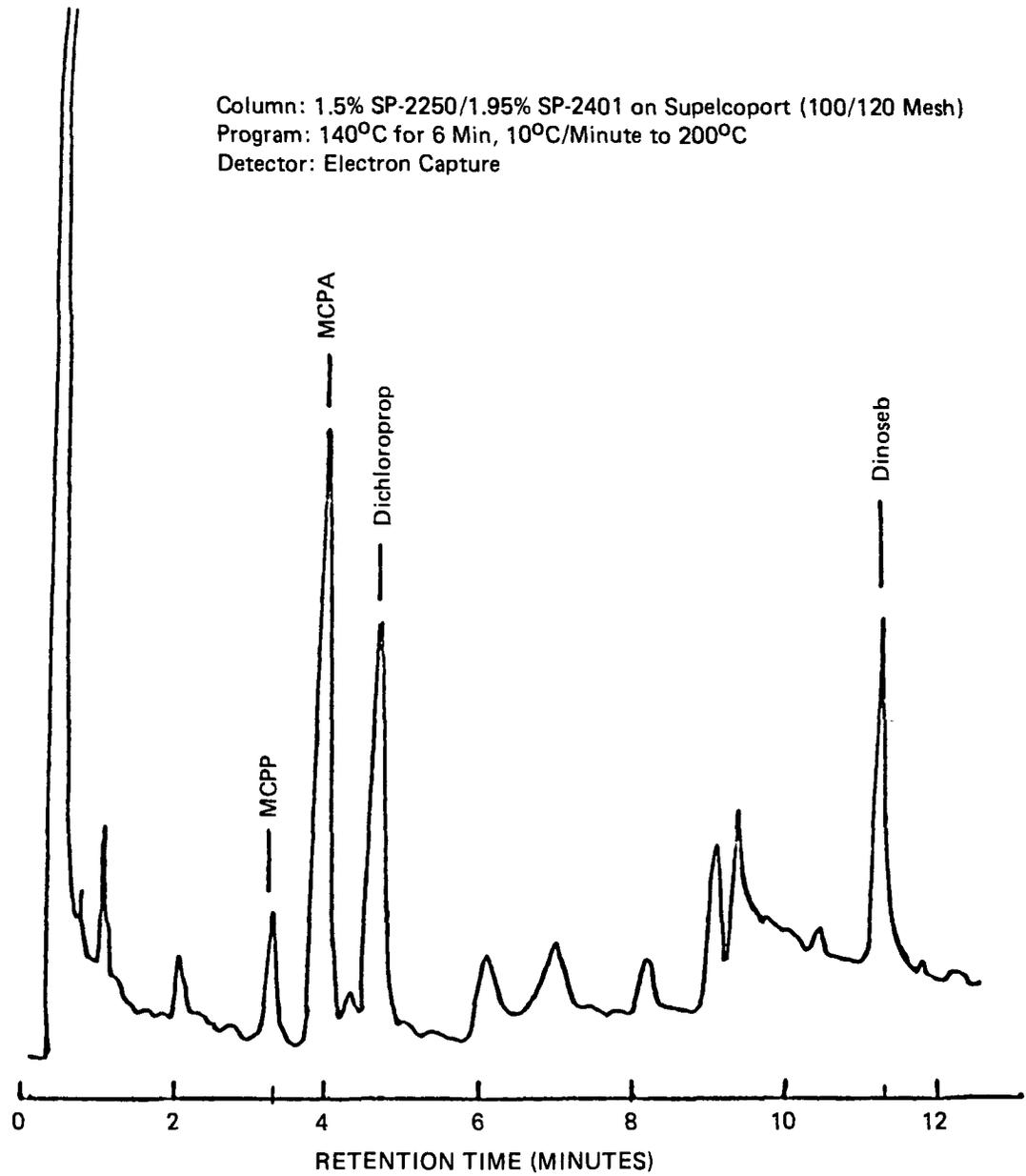


Figure 2. Gas chromatogram of chlorinated herbicides.

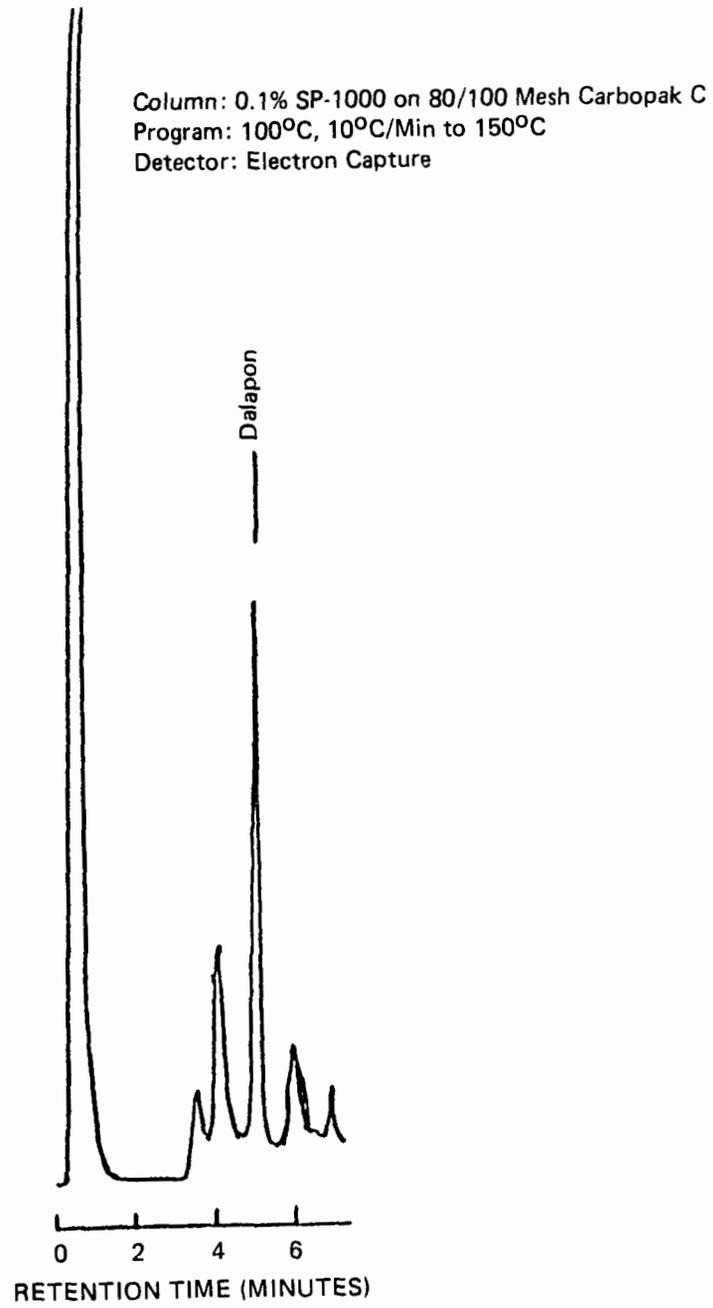


Figure 3. Gas chromatogram of dalapon, column 3.

the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified waste samples should be analyzed to validate the accuracy of the analysis. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry should be used (Section 8.3).

### 8.3 GC/MS confirmation

8.3.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The mass spectrometer should be capable of scanning the mass range from 35 amu to a mass 50 amu above the molecular weight of the compound. The instrument must be capable of scanning the mass range at a rate to produce at least 5 scans per peak but not to exceed 3 sec per scan utilizing 70 V (nominal) electron energy in the electron impact ionization mode. A GC-to-MS interface constructed of all-glass or glass-lined materials is recommended. A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program should be interfaced to the mass spectrometer.

8.3.2 Gas chromatographic columns and conditions should be selected for optimum separation and performance. The conditions selected must be compatible with standard GC/MS operating practices, such as those described for Method 8250.

8.3.3 At the beginning of each day that confirmatory analyses are to be performed, the GC/MS system must be checked to see that all DFTPP (decafluorotriphenyl phosphine) performance criteria are achieved, as described in Method 8250.

8.3.4 To confirm an identification of a compound, the background-corrected mass spectrum of the compound must be obtained from the sample extract and compared with a mass spectrum from a stock or calibration standard analyzed under the same chromatographic conditions. At least 25 ng of material should be injected into the GC/MS. The following criteria must be met for qualitative confirmation:

1. The molecular ion and all other ions present above 10% relative abundance in the mass spectrum of the standard must be present in the mass spectrum of the sample with agreement to  $\pm 10\%$ . For example, if the relative abundance of an ion is 30% in the mass spectrum of the standard, the allowable limits for the relative abundance of that ion in the mass spectrum for the sample would be 20-40%.

2. The retention time of the compound in the sample must be within 6 sec of the retention time for the same compound in the standard solution.
3. Compounds that have very similar mass spectra can be explicitly identified by GC/MS only on the basis of retention time data.

8.3.5 Where available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.3.6 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

## 9.0 References

1. U.S. EPA. 1971. National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio.
2. Goerlitz, D.G., and W.L. Lamar. 1967. Determination of phenoxy acid herbicides in water by electron capture and microcoulometric gas chromatography. U.S. Geol. Survey Water Supply Paper, 1817-C.
3. Burke, J.A., 1965. Gas chromatography for pesticide residue analysis; some practical aspects. Journal of the Association of Official Analytical Chemists 48:1037.
4. U.S. EPA. 1972. Extraction and cleanup procedure for the determination of phenoxy acid herbicides in sediment. EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi.

## 8.2 Gas Chromatographic/Mass Spectroscopy Methods (8200 series)

Methods appropriate for organic analysis by GC/MS methods are included on the following pages.

## METHOD 8240

### GC/MS METHOD FOR VOLATILE ORGANICS

#### 1.0 Scope and Application

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 The detection limit of Method 8240 for an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples containing more than 1 mg/g of total volatile material, the detection limit is proportionately higher.

1.3 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by or under the supervision of analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra and their use as a quantitative tool.

#### 2.0 Summary of Method

2.1 The volatile compounds are introduced to the gas chromatograph by direct injection, the Headspace Method (Method 5020), or the Purge-and-Trap Method (Method 5030). Method 5030 should be used for groundwater analysis. 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.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample can be dispersed in methanol or polyethylene glycol (PEG) to dissolve the volatile organic constituents. A portion of the methanolic or PEG solution is combined with water in a specially designed purging chamber. An inert gas is then bubbled through the solution at ambient temperature and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

2.3 An aliquot of each sample must be spiked with an appropriate standard to determine percent recovery and detection limits for that sample.

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2.4 Table 1 lists detection limits that can be obtained in wastewaters in the absence of interferences. Detection limits for a typical waste sample would be significantly higher.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention time (min) Column 1 <sup>a</sup>	Method detection limit (µg/l)
Chloromethane	2.3	ND
Bromomethane	3.1	ND
Vinyl chloride	3.8	ND
Chloroethane	4.6	ND
Methylene chloride	6.4	2.8
Trichlorofluoromethane	8.3	ND
1,1-Dichloroethene	9.0	2.8
1,1-Dichloroethane	10.1	4.7
trans-1,2-Dichloroethene	10.8	1.6
Chloroform	11.4	1.6
1,2-Dichloroethane	12.1	2.8
1,1,1-Trichloroethane	13.4	3.8
Carbon tetrachloride	13.7	2.8
Bromodichloromethane	14.3	2.2
1,2-Dichloropropane	15.7	6.0
trans-1,3-Dichloropropene	15.9	5.0
Trichloroethene	16.5	1.9
Benzene	17.0	4.4
Dibromochloromethane	17.1	3.1
1,1,2-Trichloroethane	17.2	5.0
cis-1,3-Dichloropropene	17.2	ND
2-Chloroethylvinyl ether	18.6	ND
Bromoform	19.8	4.7
1,1,2,2-Tetrachloroethane	22.1	6.9
Tetrachloroethene	22.2	4.1
Toluene	23.5	6.0
Chlorobenzene	24.6	6.0
Ethyl benzene	26.4	7.2
1,3-Dichlorobenzene	33.9	ND
1,2-Dichlorobenzene	35.0	ND
1,4-Dichlorobenzene	35.4	ND

ND = not determined.

<sup>a</sup>Column conditions: Carbowack B (60/80 mesh) coated with 1% SP-1000 packed in a 6-ft by 2-mm I.D. glass column with helium carrier gas at a flow rate of 30 ml/min. Column temperature is isothermal at 45° C for 3 min, then programmed at 8° C per minute to 220° and held for 15 min.

### 3.0 Interferences

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the particular waste or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences under the conditions of the analysis by running method blanks. Method blanks are run by analyzing organic-free water in the 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, 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 Low molecular weight impurities in PEG can be volatilized during the purging procedure. Thus, the PEG employed in this method must be purified before use as described in Section 5.2.

### 4.0 Apparatus and Materials

#### 4.1 Sampling equipment

4.1.1 Vial: 25-ml capacity or larger, equipped with a screw cap (Pierce #13075 or equivalent). Detergent wash, rinse with tap and distilled water, and dry for 1 hr 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 1 hr before use.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the purging chamber, trap, and the desorber. Several complete devices are now commercially available.

4.2.1 The purging chamber must be designed to accept 5-ml or 25-ml samples with a water column at least 3 cm deep. The gaseous head space between the water column and the trap must have a total volume of less than 15 ml. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The purging chamber, illustrated in Figure 1, meets these design criteria.

4.2.2 The trap must be at least 25 cm long and have an inside diameter of at least 2.5 mm. The trap must be packed to contain the following minimum lengths-of-adsorbents: 1.0 cm of methyl-silicone-coated packing (Section 5.3.2), 15 cm of 2,6-diphenylene oxide polymer (Section 5.3.1), and 8 cm of silica gel (Section 5.3.3). The minimum specifications for the trap are illustrated in Figure 2.

4.2.3 The desorber must be capable of rapidly heating the trap to 180° C within 30 sec. The polymer section of the trap should not be heated higher than 180° C and the remaining sections should not exceed 220° C. The desorber design, illustrated in Figure 2, meets these criteria.

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

#### 4.3 Gas chromatograph/mass spectrometer system

4.3.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Column: 2-m x 2-mm I.D. stainless steel or glass, packed with 1% SP-1000 on 60/80 mesh Carboxen B or equivalent.

4.3.3 Mass spectrometer: Capable of scanning from 40 to 250 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of 4-bromofluorobenzene (BFB) is injected through the GC inlet or introduced in the purge-and-trap mode.

4.3.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Section 9) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

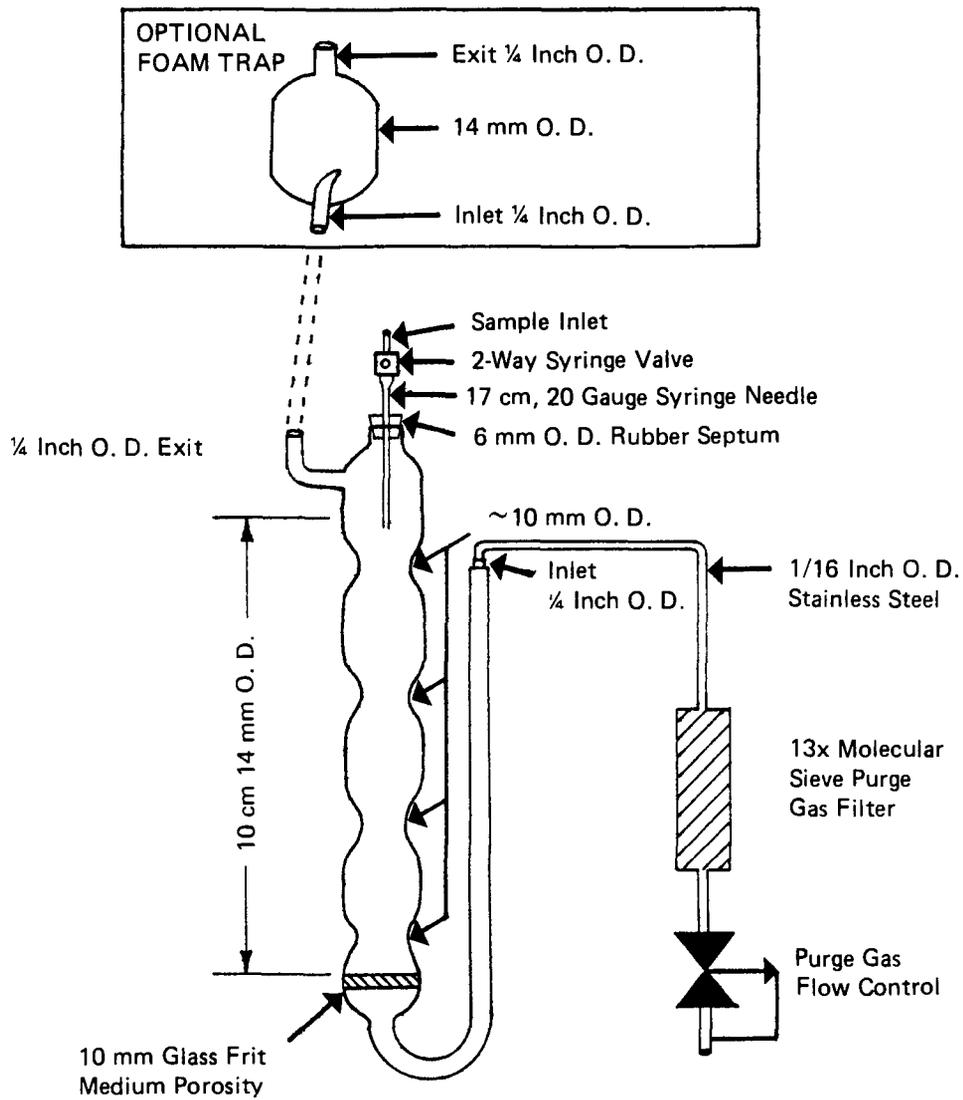


Figure 1. Purging chamber.

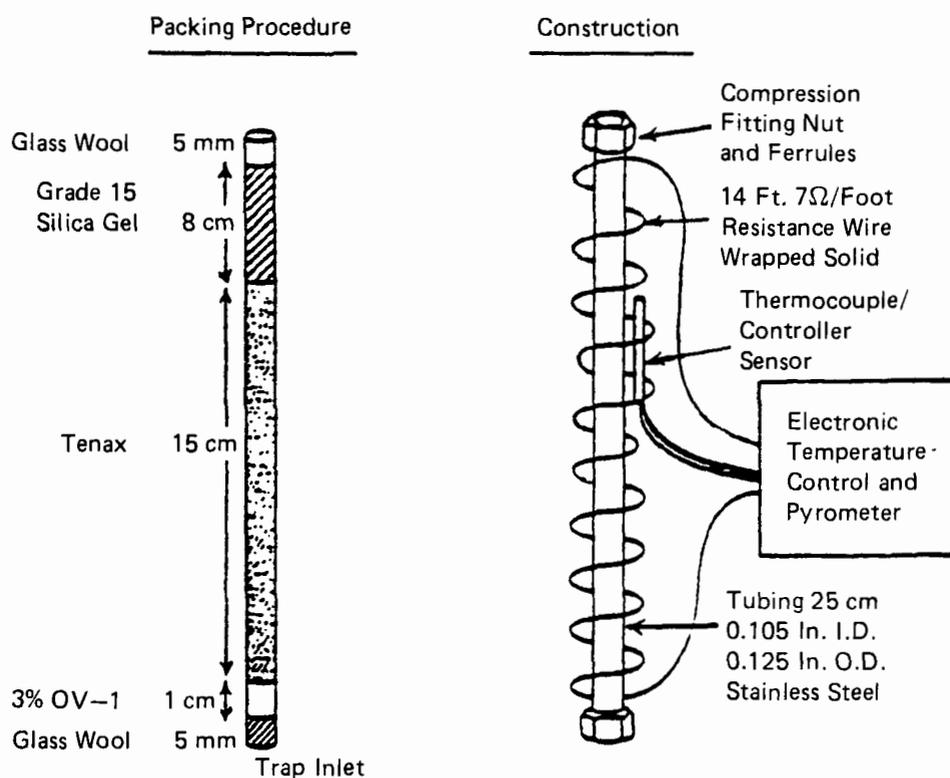


Figure 2. Trap packings and construction to include desorb capability.

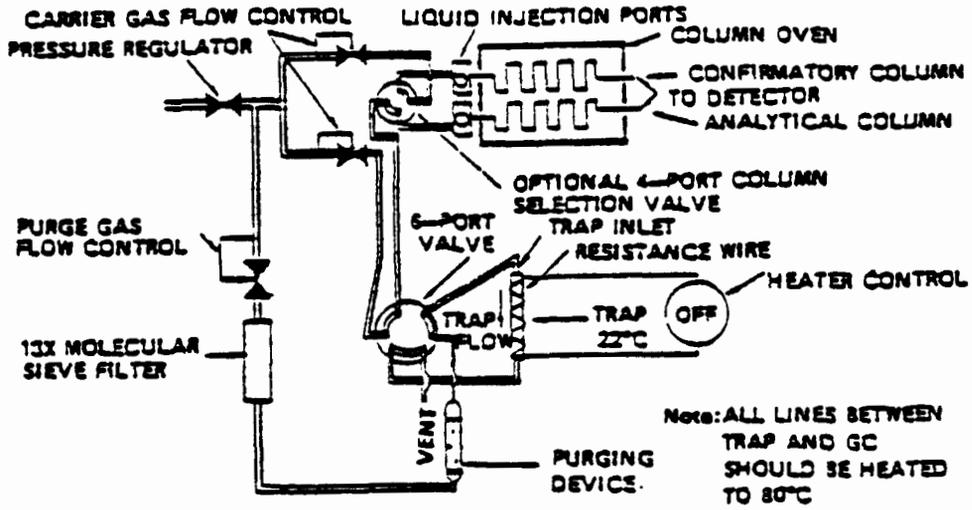


FIGURE 3. Schematic of purge and trap device - purge mode

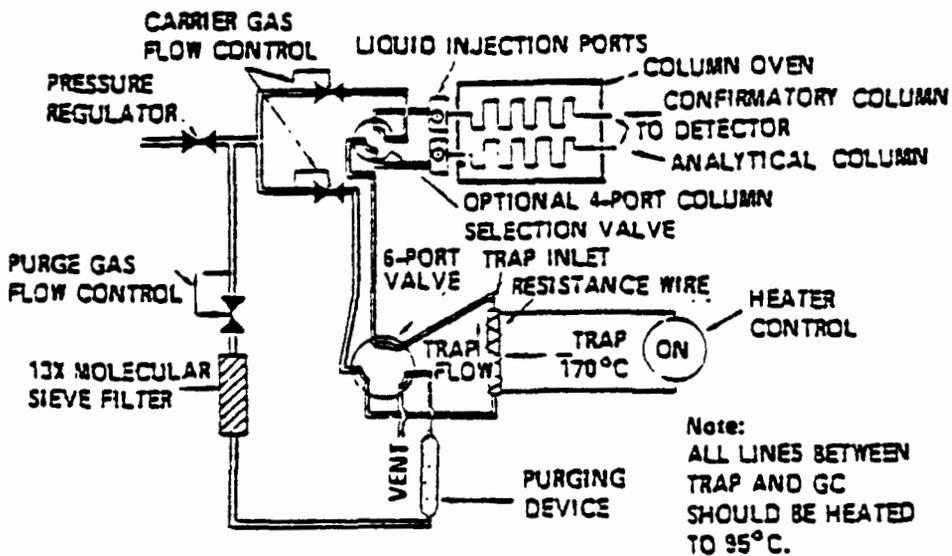


Figure 4. Schematic of purge and trap device - desorb mode

4.3.5 Data system: A computer system must be interfaced to the mass spectrometer that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that allows searching any GC/MS data file for ions of a specific mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits. Hardware and software must be available to transform the data into a compatible format. These generally consist of a 9-inch, 800-bpi tape drive and the associated software.

4.4 Sample transfer implements: Implements are required to transfer portions of solid, semisolid, and liquid wastes from sample containers to laboratory glassware. The transfer must be accomplished rapidly to avoid loss of volatile components during the transfer step. Liquids may be transferred using a hypodermic syringe with a wide-bore needle or no needle attached. Samples should be introduced into the syringe by (1) removing the plunger from the syringe, (2) pouring the sample into the barrel, and (3) replacing the barrel and inverting the syringe to remove any air trapped in the syringe. Do not draw the sample up into the syringe. Solids may be transferred using a conventional laboratory spatula, spoon, or coring device. A coring device that is suitable for handling some samples can be made by using a glass tubing saw to cut away the closed end of the barrel of a glass hypodermic syringe.

TABLE 2. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion abundance criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	Base Peak, 100% Relative Abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 100% of mass 174
177	5 to 9% of mass 176

4.5 Syringes: 5-ml and 25-ml glass hypodermic, equipped with 20-gauge needle, at least 15 cm in length.

4.6 Micro syringes: 10- $\mu$ l, 25- $\mu$ l, 100- $\mu$ l, 250- $\mu$ l, and 1000- $\mu$ l. These syringes should be equipped with 20-gauge needles having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device (see Figure 1). The needle length required will depend upon the dimensions of the purging device employed.

4.7 Centrifuge tubes: 50-ml round-bottom glass centrifuge tubes with Teflon-lined screw caps. The tubes must be marked before use to show an approximate 20-ml graduation.

4.8 Centrifuge: Capable of accommodating 50-ml glass tubes.

4.9 Syringe valve: 2-way, with Luer ends (2 each) (Hamilton #86725 valve equipped with one Hamilton #35033 Luer fitting, or equivalent).

4.10 Syringe: 5-ml, gas-tight with shut-off valve.

4.11 Bottle: 15-ml, screw-cap, Teflon cap liner.

4.12 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.13 Rotary evaporator: equipped with Teflon-coated seals (Buchi Rotavapor R-110, or equivalent).

4.14 Vacuum pump: mechanical, two-stage.

## 5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300, or equivalent).

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

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

5.1.4 Reagent water may also be purchased under the name "HPLC water" from several manufacturers (Burdick and Jackson, Baker and Waters, Inc.).

5.2 Reagent PEG: Reagent PEG is defined as PEG having a nominal average molecular weight of 400, and in which interferences are not observed at the method detection limit for compounds of interest.

5.2.1 Reagent PEG is prepared by purification of commercial PEG having a nominal average molecular weight of 400. The PEG is placed in a round-bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100° C and vacuum is maintained at less than 10 mm Hg for at least 1 hr using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the PEG, a reagent water/PEG blank must be analyzed.

### 5.3 Trap materials

5.3.1 2,6-Diphenylene oxide polymer: 60/80-mesh Tenax, chromatographic grade or equivalent.

5.3.2 Methyl silicone packing: 3 percent OV-1 on 60/80 mesh Chromosorb-W or equivalent.

5.3.3 Silica gel, Davison Chemical (35/60 mesh), grade-15 or equivalent.

5.3.4 Prepared trapping columns may be purchased from several chromatography suppliers.

5.4 Methanol: Distilled-in-glass quality or equivalent.

5.5 Calibration standards; stock solutions (2 mg/ml): Stock solutions of calibration standards may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions of individual compounds 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 by analysts when handling high concentrations of these materials.

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

5.5.2 Add the assayed reference material as described below.

5.5.2.1 Liquids: Using a 100- $\mu$ l syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30° C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-ml valved gas-tight syringe with a reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol.

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

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

5.5.5 Prepare fresh standards weekly for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after one month, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards; secondary dilution solutions: Using stock solutions described in Section 5.5, prepare secondary dilution standards in methanol that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the methanol or aqueous PEG calibration solutions prepared as described in Section 6.3.2 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace and should be checked frequently for signs of evaporation, especially just prior to preparing calibration standards from them.

5.7 Surrogate standards: Surrogate standards may be added to samples and calibration solutions to assess the effect of the sample matrix on recovery efficiency. The compounds employed for this purpose are 1,2-dibromotetrafluoroethane, bis(perfluoroisopropyl) ketone, fluorobenzene, and *m*-bromobenzotrifluoride. Prepare methanolic solutions of the surrogate standards using the procedures described in Sections 5.5 and 5.6. The

concentrations prepared and the amount of solution added to each sample should be those required to give an amount of each surrogate in the purging device that is equal to the amount of each internal standard added, assuming a 100% recovery of the surrogate standards.

5.8 Internal standards: In this method, internal standards are employed during analysis of all samples and during all calibration procedures. The analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. However, for general use, D<sub>4</sub>-1,2-dichloroethane, D<sub>6</sub>-benzene, and D<sub>5</sub>-ethylbenzene are recommended as internal standards covering a wide boiling point range.

5.9 4-Bromofluorobenzene (BFB): BFB is added to the internal standard solution or analyzed alone to permit the mass spectrometer tuning for each GC/MS run to be checked.

5.10 Internal standard solution: Using the procedures described in Sections 5.5 and 5.6, prepare a methanolic solution containing each internal standard at a concentration of 12.5 µg/ml.

5.11 Sodium monohydrogen phosphate: 2.0 µ in distilled water.

5.12 n-Nonane and n-dodecane, 98+% purity.

5.13 N-Hexadecane, distilled-in-glass (Burdick and Jackson, or equivalent).

## 6.0 Sample Collection, Handling, and Preservation

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples must be stored in Teflon-lined screw cap vials. Sample containers should be filled as completely as possible so as to minimize headspace or void space. Vials containing liquid sample should be stored in an inverted position.

6.3 All samples must be iced or refrigerated from the time of collection to the time of analysis, and should be protected from light.

## 7.0 Procedure

### 7.1 Calibration

7.1.1 Assemble a purge-and-trap device that meets the specifications in Section 4.2 and connect the device to a GC/MS system. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, condition the trap daily for 10 min while backflushing at 180° C.

7.1.2 Operate the gas chromatograph using the conditions described in Section 7.3.5 and operate the mass spectrometer using the conditions described in Section 7.3.2.

#### 7.1.3 Calibration procedure

7.1.3.1 Conduct calibration procedures using a minimum of three concentration levels for each calibration standard. One of the concentration levels should be at a concentration near but above the method detection limit. The remaining two concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3.2 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. To the purging device, add 5.0 ml of reagent water or reagent water/PEG solution. This solution is prepared by taking 4.0 ml of reagent water or reagent PEG and diluting to 100 ml with reagent water. The reagent water/PEG solution is added to the purging device using a 5-ml glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of a 20-gauge needle. Next, using a 10- $\mu$ l or 25- $\mu$ l micro-syringe equipped with a long needle (see Section 4.6), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (see Section 5.6). Add the aliquot of calibration solution directly to the reagent water or reagent water/PEG solution in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe be sure that the end of the syringe needle is well beneath the surface of the reagent water or water/PEG solution. Similarly, add 20  $\mu$ l of the internal standard solution (see Section 5.10). Close the 2-way syringe valve at the sample inlet.

7.1.3.3 Carry out the purge and analysis procedure as described in Section 7.3.4. Tabulate the area response of the primary characteristic ion against concentration for each compound

including the internal standards. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

$A_S$  = Area of the primary characteristic ion for the compound to be measured

$A_{IS}$  = Area of the primary characteristic ion of the internal standard

$C_{IS}$  = Concentration of the internal standard

$C_S$  = Concentration of the compound to be measured.

The internal standard selected for the calculation of the RF of a compound and subsequent quantification of the compound is generally the internal standard that has a retention time closest to that of the compound. It is assumed that a linear calibration plot will be obtained over the range of concentrations used. If the RF value over the working range is a constant (less than 10% relative standard deviation), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{IS}$ , versus RF.

7.1.3.4 The RF must be verified on each working day. The concentrations selected should be near the midpoint of the working range. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within  $\pm 20\%$  of the response factor used for quantification of the sample concentrations.

## 7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for BFB (see Table 2).

7.2.2 The BFB performance test requires the following instrumental parameters:

Electron Energy: 70 volts (nominal)

Mass Range: 40 to 250 amu

Scan Time: to give approximately 6 scans per peak but not to exceed 3 sec per scan.

7.2.3 Bleed BFB vapor into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of BFB given in Table 1. A solution containing 20 ng of BFB may be injected onto the gas chromatographic column in order to check the key ion criteria.

7.2.4 The peak intensity of D<sub>6</sub>-benzene is used to monitor the mass spectrometer sensitivity. The peak intensity for D<sub>6</sub>-benzene observed during each sample analysis must be between 0.7 and 1.4 times the D<sub>6</sub>-benzene peak intensity observed during the applicable calibration runs. For example, if the peak intensity of D<sub>6</sub>-benzene observed during calibration was 355,000 area counts, then each subsequent sample or blank must give a D<sub>6</sub>-benzene peak intensity of between 250,000 and 500,000 area counts. If the D<sub>6</sub>-benzene peak intensity is outside the specified range, the sample must be reanalyzed. If the peak intensity is again outside the specified range, the analyst must investigate the cause of the variability in sensitivity and correct the problem.

### 7.3 Sample extraction and analysis

7.3.1 The analytical procedure involves extracting the non-aqueous sample with methanol or polyethylene glycol (PEG) and analyzing a portion of the extract by a purge-and-trap GC/MS procedure. The amount of the extract to be taken for the GC/MS analysis is based on the estimated total volatile content (TVC) of the sample. The TVC is estimated by extracting the sample with n-hexadecane and analyzing the n-hexadecane extract by gas chromatography.

7.3.2 The estimated TVC is based on the total area response relative to that of n-nonane for all components eluting prior to the retention time of n-dodecane. The response factor for n-nonane and the retention time of n-dodecane are determined by analyzing a 2- $\mu$ l aliquot of an n-hexadecane solution containing 0.20 mg/ml of n-nonane and n-dodecane.

7.3.2.1 The GC analyses are conducted using a flame ionization detector and a 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100-200 mesh Chromosorb W-HP. The column temperature is programmed from 80° C to 280° C at 8°/min and held at 280° for 10 min.

7.3.2.2 Determine the area response for n-nonane and divide by 0.2 to obtain the area response factor. Record the retention time of n-dodecane.

7.3.2.3 Add 1.0 g of sample to 20 ml of n-hexadecane and 2 ml of 2.0 M Na<sub>2</sub>HPO<sub>4</sub> contained in a 50-ml glass centrifuge tube and cap securely with a Teflon-lined screw cap. Shake the mixture vigorously for one minute. If the sample does not disperse

during the shaking process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate phase separation.

7.3.2.4 Analyze a 2- $\mu$ l aliquot of the n-hexadecane supernatant using the conditions described in Section 7.3.2.1. Determine the total area response of all components eluting prior to the retention time of n-dodecane and subtract the corresponding area of an n-hexadecane blank. Using the area response factor determined for n-nonane in Section 7.3.2.2, calculate the TVC as follows:

$$\text{TVC} = \frac{\text{TAR}_{\text{sample}} - \text{TAR}_{\text{blank}}}{\text{n-Nonane Area Response Factor}} \times 20$$

where:

TVC = total volatile content of the sample in mg/g

TAR<sub>sample</sub> = total area response obtained for the sample

TAR<sub>blank</sub> = total area response obtained for a blank.

7.3.3 The transfer of an aliquot of the sample for extraction with methanol or PEG should be made as quickly as possible to minimize loss of volatiles from the sample.

7.3.3.1 To a 50-ml glass centrifuge tube with Teflon-lined cap, add 40 ml of reagent methanol or PEG. Weigh the capped centrifuge tube and methanol or PEG on an analytical balance.

7.3.3.2 Using an appropriate implement (see Section 4.4), transfer approximately 2 g of sample to the methanol or PEG in the centrifuge tube in such a fashion that the sample is dissolved in or submerged in the methanol or PEG as quickly as possible. Take care not to touch the sample-transfer implement to the methanol or PEG. Recap the centrifuge tube immediately and weigh on an analytical balance to determine an accurate sample weight.

7.3.3.3 Disperse the sample by vigorous agitation for 1 min. The mixture may be agitated manually or with the aid of a vortex-mixer. If the sample does not disperse during this process, sonify the mixture in an ultrasonic bath for 30 min. Allow the mixture to stand until a clear supernatant is obtained as the sample extract. Centrifuge if necessary to facilitate phase separation.

7.3.3.4 The sample extract may be stored for future analytical needs. If this is desired, transfer the solution to a 10-ml screw cap vial with Teflon cap liner. Store at -10 to -20° C, and protect from light.

7.3.4 Reagent water, internal standard solution, and the sample extract are added to a purging chamber that is connected to the purge-and-trap device and that has been flushed with helium during a 7-min trap reconditioning step (see Section 7.3.4.4). The additions are made using an appropriately sized syringe equipped with a 15-cm 20-gauge needle. Open the syringe valve of the sample inlet (shown in Figure 1) and insert the needle through the valve.

7.3.4.1 Add 5.0 ml of reagent water or aqueous sample to which 20.0  $\mu$ l of the internal standard solution has been added (see Section 5.10) to the purging chamber. Insert the needle of the syringe well below the surface of the water for the addition of the internal standard solution. If the sample is aqueous go to Section 7.3.5.

7.3.4.2 Add an aliquot of the sample extract from Section 7.3.3.4. The total quantity of volatile components injected should not exceed approximately 10  $\mu$ g. If the total volatile content (TVC) of the sample as determined in Section 7.3.1.4 is 1.0 mg/g or less, use a 200- $\mu$ l aliquot of the sample extract. If the TVC is greater than 1.0 mg/g, use an aliquot of the sample extract that contains approximately 10  $\mu$ g of total volatile components; the volume (in  $\mu$ l) of the aliquot to be taken can be calculated by dividing 200 by the TVC. If the TVC is greater than 20 mg/g, take a 500- $\mu$ l aliquot of the sample extract and dilute to 10 ml with PEG. In this case calculate the aliquot volume (in  $\mu$ l) of the undiluted extract to be taken by dividing 4,000 by the TVC. If the TVC is less than 1.0 mg/g and greater sensitivity is desired, use a large purging chamber containing 25 ml of reagent water and use a 1.0-ml aliquot of the sample extract.

7.3.4.3 Close the 2-way syringe valve at the sample inlet.

7.3.5 The sample in the purging chamber is purged with helium to transfer the volatile components to the trap. The trap is then heated to desorb the volatile components which are swept by the helium carrier gas onto the GC column for analysis.

7.3.5.1 Adjust the gas (helium) flow rate to  $40 \pm 3$  ml/min. Set the purging device to purge, and purge the sample for  $11.0 \pm 0.1$  min at ambient temperature.

7.3.5.2 At the conclusion of the purge time, adjust the device to the desorb mode, and begin the GC/MS analysis and data acquisition using the following GC operating conditions:

Column: 6-ft x 2-mm I.D. glass column of 1% SP-1000 on Carbo-pack B (60-80 mesh).

Temperature: Isothermal at 45° C for 3 min, then increased at 8° C/min to 220° C, and maintained at 220° C for 15 min.

Concurrently, introduce the trapped materials to the GC column by rapidly heating the trap to 180° C while backflushing the trap with helium at a flow rate of 30 ml/min for 4 min. If this rapid heating requirement cannot be met, the GC column must be used as a secondary trap by cooling it to 30° C or lower during the 4-min desorb step and starting the GC program after the desorb step.

7.3.5.3 Return the purge-and-trap device to the purge mode and continue acquiring GC/MS data.

7.3.5.4 Allow the trap to cool for 8 min. Replace the purging chamber with a clean purging chamber. The purging chamber is cleaned after each use by sequential washing with acetone, methanol, detergent solution and distilled water, and then dried at 105° C.

7.3.5.5 Close the syringe valve on the purging chamber after 15 sec to begin gas flow through the trap. Purge the trap at ambient temperature for 4 min. Recondition the trap by heating it to 180° C. Do not allow the trap temperature to exceed 180° C, since the sorption/desorption is adversely affected when the trap is heated to higher temperatures. After heating the trap for approximately 7 min, turn off the trap heater. When cool, the trap is ready for the next sample.

7.3.6 If the response for any ion exceeds the working range of the system, repeat the analysis using a correspondingly smaller aliquot of the sample extract described in Section 7.3.2.3.

#### 7.4 Qualitative identification

7.4.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.4.1.1 The characteristic ions of each compound of interest must maximize in the same or within one scan of each other.

7.4.1.2 The retention time must fall within  $\pm 30$  sec of the retention time of the authentic compound.

7.4.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within  $\pm 20\%$  of the relative intensities of these ions in a reference mass spectrum. Reference spectra may be generated from the standards analyzed by the analyst or from a reference library. All reference spectra generated from standards must be obtained from an appropriately tuned mass spectrometer.

## 7.5 Quantitative determination

7.5.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion, as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used. Generally, the base peak of the mass spectrum is used.

## 8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of the data that are generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.1.3 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. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methanol at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples by adding the spiking solution to the PEG used for the extraction. Analyze the spiked aliquots according to the method in Section 7.3.

8.2.4 Calculate the average percent recovery,  $R$ , and the standard deviation of the percent recovery,  $s$ , for all compounds and surrogate standards. Background corrections must be made before  $R$  and  $s$  calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery,  $s/R \times 100$ , must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for  $R$  and  $s$  calculated in Section 8.2.4:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= R + 3s \\ \text{Lower Control Limit (LCL)} &= R - 3s\end{aligned}$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the  $R$  and  $s$  values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standards to monitor spike recoveries. The spiking level used should be that which will give an amount in the purge apparatus that is equal to the amount of the internal standard assuming a 100% recovery of the surrogate standards. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be

qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Four surrogate standards, namely 1,2-dibromodifluoroethane, bis(perfluoroisopropyl) ether, fluorobenzene, and m-bromobenzotrifluoride, are recommended for general use to monitor recovery of volatile compounds varying in volatility and polarity.

8.5 Each day, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.8 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.9 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 3 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 3.

TABLE 3. ACCURACY AND PRECISION FOR PURGEABLE ORGANICS

Parameter	Reagent Water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Benzene	99	9	98	10
Bromodichloromethane	102	12	103	10
Bromoform	104	14	105	16
Bromomethane	100	20	88	23
Carbon tetrachloride	102	16	104	15
Chlorobenzene	100	7	102	9
Chloroethane	97	22	103	31
2-Chloroethyl vinyl ether	101	13	95	17
Chloroform	101	10	101	12
Chloromethane	99	19	99	24
Dibromochloromethane	103	11	104	14
1,1-Dichloroethane	101	10	104	15
1,2-Dichloroethane	100	8	102	10
1,1-Dichloroethene	102	17	99	15
trans-1,2-Dichloroethene	99	12	101	10
1,2-Dichloropropane	102	8	103	12
cis-1,3-Dichloropropene	105	15	102	19
trans-1,3-Dichloropropene	104	11	100	18
Ethyl benzene	100	8	103	10
Methylene chloride	96	16	89	28
1,1,2,2-Tetrachloroethane	102	9	104	14
Tetrachloroethene	101	9	100	11
Toluene	101	9	98	14
1,1,1-Trichloroethane	101	11	102	16
1,1,2-Trichloroethane	101	10	104	15
Trichloroethene	101	9	100	12
Trichlorofluoromethane	103	11	107	19
Vinyl chloride	100	13	98	25

Samples were spiked between 10 and 1000 µg/l.

## METHOD 8250

### GC/MS METHOD FOR SEMIVOLATILE ORGANICS: PACKED COLUMN TECHNIQUE

#### 1.0 Scope and Application

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds (see Tables 1 and 2) in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including groundwater, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8250 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8250 for determining an individual compound is approximately 1 µg/g (wet weight) in waste samples. For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8250 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), acid base extraction (Method 3530), sonication (Method 3550), or soxhlet extraction (Method 3540). For groundwater samples Method 3530 should be used. If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Retention time (min)	Method detection limit ( $\mu\text{g/l}$ )	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
1,3-Dichlorobenzene	7.4	1.9	146	148	113	146	148	150
1,4-Dichlorobenzene	7.8	4.4	146	148	113	146	148	150
Hexachloroethane	8.4	1.6	117	201	199	199	201	203
Bis(2-chloroethyl) ether	8.4	5.7	93	63	95	63	107	109
1,2-Dichlorobenzene	8.4	1.9	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	9.3	5.7	45	77	79	77	135	137
N-Nitrosodi-n-propyl amine			130	42	101			
Nitrobenzene	11.1	1.9	77	123	65	124	152	164
Hexachlorobutadiene	11.4	0.9	225	223	227	223	225	227
1,2,4-Trichlorobenzene	11.6	1.9	180	182	145	181	183	209
Isophorone	11.9	2.2	82	95	138	139	167	178
Naphthalene	12.1	1.6	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	12.2	5.3	93	95	123	65	107	137
Hexachlorocyclopentadiene	13.9		237	235	272	235	237	239
2-Chloronaphthalene	15.9	1.9	162	164	127	163	191	203
Acenaphthylene	17.4	3.5	152	151	153	152	153	181
Acenaphthene	17.8	1.9	154	153	152	154	155	183
Dimethyl phthalate	18.3	1.6	163	194	164	151	163	164
2,6-Dinitrotoluene	18.7	1.9	165	89	121	183	211	223
Fluorene	19.5	1.9	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	19.5	4.2	204	206	141			
2,4-Dinitrotoluene	19.8	5.7	165	63	182	183	211	223
Diethylphthalate	20.1	22	149	177	150	177	223	251
N-Nitrosodiphenylamine	20.5	1.9	169	168	167	169	170	198
Hexachlorobenzene	21.0	1.9	284	142	249	284	286	288
$\alpha$ -BHC	21.1		183	181	109			
4-Bromophenyl phenyl ether	21.2	1.9	248	250	141	249	251	277
$\gamma$ -BHC	22.4		183	181	109			

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
Phenanthrene	22.8	5.4	178	179	176	178	179	207
Anthracene	22.8	1.9	178	179	176	178	179	207
β-BHC	23.4	4.2	181	183	109			
Heptachlor	23.4	1.9	100	272	274			
δ-BHC	23.7	3.1	183	109	181			
Aldrin	24.0	1.9	66	263	220			
Dibutyl phthalate	24.7	2.5	149	150	104	149	205	279
Heptachlor epoxide	25.6	2.2	353	355	351			
Endosulfan I	26.4	--	237	339	341			
Fluoranthene	26.5	2.2	202	101	100	203	231	243
Dieldrin	27.2	2.5	79	263	279			
4,4'-DDE	27.2	5.6	246	248	176			
Pyrene	27.3	1.9	202	101	100	203	231	243
Endrin	27.9	--	81	263	82			
Endosulfan II	28.6	--	237	339	341			
4,4'-DDD	28.6	2.8	235	237	165			
Benzidine	28.8	44	184	92	185	185	213	225
4,4'-DDT	29.3	4.7	235	237	165			
Endosulfan sulfate	29.8	5.6	272	387	422			
Endrin aldehyde	--	--	67	345	250			
Butyl benzyl phthalate	29.9	2.5	149	91	206	149	299	327
Bis(2-ethylhexyl) phthalate	30.6	2.5	149	167	279	149		
Chrysene	31.5	2.5	228	226	229	228	229	257
Benzo(a)anthracene	31.5	7.8	228	229	226	228	229	257
3,3'-Dichlorobenzidine	32.2	16.5	252	254	126			
Di-n-octyl phthalate	32.5	2.5	149					
Benzo(b)fluoranthene	34.9	4.8	252	253	125	252	253	281
Benzo(k)fluoranthene	34.9	2.5	252	253	125	252	253	281
Benzo(a)pyrene	36.4	2.5	252	253	125	252	253	281

TABLE 1. (CONT.)

Parameter	Retention time (min)	Method detection limit ( $\mu\text{g/l}$ )	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
Indeno(1,2,3-c,d)pyrene	42.7	3.7	276	138	277	276	277	305
Dibenzo(a,h)anthracene	43.2	2.5	278	139	279	278	279	307
Benzo(ghi)perylene	45.1	4.1	276	138	277	276	277	305
N-Nitrosodimethyl amine	--	--	42	74	44			
Chlordane <sup>a</sup>	19 to 30	--	373	375	377			
Toxaphene <sup>a</sup>	25 to 34	--	159	231	233			
PCB 1016 <sup>a</sup>	18 to 30	--	224	260	294			
PCB 1221 <sup>a</sup>	15 to 30	30	190	224	260			
PCB 1232 <sup>a</sup>	15 to 32	--	190	224	260			
PCB 1242 <sup>a</sup>	15 to 32	--	224	260	294			
PCB 1248 <sup>a</sup>	12 to 34	--	294	330	362			
PCB 1254 <sup>a</sup>	22 to 34	36	294	330	362			
PCB 1260 <sup>a</sup>	23 to 32	--	330	362	394			

<sup>a</sup>These compounds are mixtures of various isomers (See Figures 2 to 12).

Gas chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 3% SP-2250. Carrier gas: helium at a flow rate of 30 ml/min. Temperature: Isothermal at 50° C for 4 min, then 8° per min to 270° C. Hold at 270° C for 30 min.

TABLE 2. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR ACID EXTRACTABLES

Parameter	Retention time (min)	Method detection limit (µg/l)	Characteristic ions					
			Electron impact			Chemical ionization (methane)		
			Primary	Secondary				
2-Chlorophenol	5.9	3.3	128	64	130	129	131	157
2-Nitrophenol	6.5	3.6	139	65	109	140	168	122
Phenol	8.0	1.5	94	65	66	95	123	135
2,4-Dimethylphenol	9.4	2.7	122	107	121	123	151	163
2,4-Dichlorophenol	9.8	2.7	162	164	98	163	165	167
2,4,6-Trichlorophenol	11.8	2.7	196	198	200	197	199	201
4-Chloro-3-methylphenol	13.2	3.0	142	107	144	143	171	183
2,4-Dinitrophenol	15.9	42	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	16.2	24	198	182	77	199	227	239
Pentachlorophenol	17.5	3.6	266	264	268	267	265	269
4-Nitrophenol	20.3	2.4	65	139	109	140	168	122

Chromatographic conditions: Glass column 1.8 m long x 2 mm I.D. packed with Supelcoport (100/120) coated with 1% SP-1240 DA. Carrier gas: helium at a flow rate of 30 ml/min. Column temperature, isothermal at 70° C for 2 min, then 8° per min to 200° C.

### 3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All 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 waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

### 4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

#### 4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

#### 4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon Luerlock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- $\mu$ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- $\mu$ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to  $\pm 0.1$  pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

## 4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column for base-neutral compounds: 2-m x 2-mm I.D. stainless steel or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport B or equivalent.

4.15.3 Column for acidic compounds: 2-m x 2-mm I.D. glass packed with 1% SP 1240-DA on 100/120 mesh Supelcoport.

4.15.4 Mass spectrometer: Capable of scanning from 35 to 450 amu every 3 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 3 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA<sup>a</sup>

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

<sup>a</sup>J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

#### 4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

## 5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic ( $K_3PO_4$ ): Granular (ACS).

5.3 Phosphoric acid ( $H_3PO_4$ ): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous ( $Na_2SO_4$ ): Powder (ACS).

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

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5.6 D<sub>10</sub>-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D<sub>3</sub>-Phenol, D<sub>8</sub>-naphthalene, D<sub>10</sub>-Phenanthrene, D<sub>12</sub>-chrysene, and D<sub>12</sub>-benzo(a)pyrene. D<sub>12</sub>-perylene may be used in place of D<sub>12</sub>-benzo(a)pyrene.

5.9 Column performance standards: D<sub>3</sub>-phenol, D<sub>5</sub>-aniline, D<sub>5</sub>-nitrobenzene, and D<sub>3</sub>-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

### 7.0 Procedure

#### 7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. D<sub>10</sub>-phenanthrene is recommended for this purpose for general use. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards, and a mass spectrometer tuning standard are included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D<sub>3</sub>-phenol, D<sub>8</sub>-naphthalene, D<sub>12</sub>-chrysene, and D<sub>12</sub>-benzo(a)pyrene. D<sub>15</sub>-perylene may be substituted for D<sub>12</sub>-benzo(a)pyrene. D<sub>10</sub>-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D<sub>5</sub>-phenol, D<sub>5</sub>-aniline, D<sub>5</sub>-nitrobenzene, and D<sub>3</sub>-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

$A_s$  = Response for the parameter to be measured.

$A_{is}$  = Response for the internal standards.

$C_{is}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_s$  = Concentration of the compound to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_s/A_{is}$ , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within  $\pm 20\%$  of the response factor used for quantification of the sample concentrations.

## 7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50  $\mu\text{g/ml}$  of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% from that observed during the analysis of the calibration solution, then the analysis in question is considered invalid. The instrument

must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

### 7.3 Sample extraction

7.3.1 The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with  $\text{CH}_2$  and analyzed. Solids and semisolids are extracted by Method 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.4.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to  $7.0 \pm 0.2$  by titration with 0.4 M  $\text{H}_3\text{PO}_4$  or 0.4 M  $\text{K}_3\text{PO}_4$  using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M  $\text{H}_3\text{PO}_4$  or 4 M  $\text{K}_3\text{PO}_4$  equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M  $\text{H}_3\text{PO}_4$ , the amount of 4 M  $\text{H}_3\text{PO}_4$  needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M  $\text{H}_3\text{PO}_4$  or 4 M  $\text{K}_3\text{PO}_4$  added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing

must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- $\mu$ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire 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 min. 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 of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3 was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_s(7.3.5)} \times \frac{10}{V_c(7.3.8)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_s(7.3.8)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_s(7.3.7)} \times \frac{V_F}{V_{\text{GPC}}(7.3.7)} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

$V_s$  = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_c(7.3.8)$  = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$  = Final volume of concentrate in Section 7.3.7

$V_{\text{GPC}}$  = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

#### 7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the

above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVC of the concentrate as described in Section 7.3.6.

## 7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Method 3510, 3540, or 3550, or Section 7.3.8 by GC/MS using the appropriate column (see Section 4.15). The recommended GC operating conditions to be used are as follows:

Conditions for base neutral analysis (3% SP-2250-DB)

Initial column temperature hold: 50° C for 4 min

Column temperature program: 50-300° C at 8 degrees/min

Final column temperature hold: 300<sup>0</sup> C for 20 min.

Conditions for acid analysis (1% SP-1240-DA)

Initial column temperature: 70° C for 2 min

Column temperature program: 70-200° C at 8 degrees/min

Final column temperature hold: 200° C for 20 min

Injector temperature: 300° C

Transfer line temperature: 300° C

Sample volume: 1-2 µl

Carrier gas: Helium at 30 ml/min

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Qualitative identification. Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.2 The retention time must fall within  $\pm 15$  sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.3 The relative peak heights of the characteristic ions in the EICP's must fall within  $\pm 20\%$  of the relative intensities of these ions in a reference mass spectrum.

## 7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_S}{A_{iS}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$  = internal standard concentration factor calculated in Section 7.3.8

$A_S$  = Area of the primary characteristic ion of the compound being quantified

$A_{iS}$  = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in  $\mu\text{g/g}$  without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

## 8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery ( $R$ ) and the standard deviation of the percent recovery ( $s$ ) for all compounds and surrogate standards. Background corrections must be made before  $R$  and  $s$  calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ( $s/R \times 100$ ) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for  $R$  and  $s$  calculated in Section 8.2.4:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the  $R$  and  $s$  values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D<sub>10</sub>-phenanthrene.

8.8 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 carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 µg/g of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Tables 1 and 2. Where doubt exists over the identification of a peak on the chromatograph, confirmatory techniques such as mass spectroscopy should be used.

8.9 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Tables 1 and 2 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.10 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Tables 4 and 5 were obtained. The standard deviation of the measurement in percent recovery is also included in Tables 4 and 5.

TABLE 4. ACCURACY AND PRECISION FOR BASE/NEUTRAL EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Acenaphthene	77	23	83	29
Acenaphthylene	78	22	82	23
Aldrin	72	6	--	--
Anthracene	84	14	76	22
Benzo(a)anthracene	83	19	75	28
Benzo(b)fluoranthene	96	68	41	21
Benzo(k)fluoranthene	96	68	47	27
Benzo(ghi)perylene	80	45	68	40
Benzo(a)pyrene	90	22	43	21
Benzidine	87	61	63	55
Butyl benzyl phthalate	47	32	74	43
$\beta$ -BHC	69	25	--	--
$\delta$ -BHC	56	18	--	--
Bis (2-chloroethoxy) methane	84	33	82	74
Bis (2-chloroethyl) ether	56	36	72	37
Bis (2-chloroisopropyl) ether	71	33	71	39
Bis (2-ethylhexyl) phthalate	129	50	82	63
4-Bromophenyl phenyl ether	80	17	75	20
2-Chloronaphthalene	73	24	79	27
4-Chlorophenyl phenyl ether	45	11	--	--
Chrysene	83	19	75	28
4,4'-DDD	80	9	--	--
4,4'-DDE	69	20	--	--
4,4'-DDT	63	15	--	--
Dibenzo(a,h)anthracene	82	39	70	40
Di-n-butyl phthalate	70	25	93	51
1,2-Dichlorobenzene	59	27	62	28
1,3-Dichlorobenzene	55	28	54	24
1,4-Dichlorobenzene	61	31	63	35
3,3-Dichlorobenzidine	184	174	143	145
Diethylphthalate	42	28	48	28
Dimethyl phthalate	25	33	35	36
2,4-Dinitrotoluene	83	32	79	34
2,6-Dinitrotoluene	79	18	79	25
Di-n-octylphthalate	97	37	89	62
Endosulfan sulfate	79	29	--	--
Fluoranthene	89	19	80	26
Fluorene	77	16	80	20
Heptachlor	69	6	--	--
Heptachlor epoxide	82	7	--	--

#### 4 / ORGANIC ANALYTICAL METHODS - GC/MS

##### 4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent), with a film thickness of 0.25  $\mu$  or equivalent.

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA<sup>a</sup>

Mass	Ion abundance criteria
51	30-60% of mass 198
68	Less than 2% of mass 69
70	Less than 2% of mass 69
127	40-60% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

<sup>a</sup>J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

TABLE 4. (CONT.)

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
Hexachlorobenzene	79	20	71	22
Hexachlorobutadiene	46	25	48	28
Hexachlorocyclopentadiene	27	25	12	12
Hexachloroethane	46	21	52	26
Indeno (1,2,3-cd) pyrene	65	37	81	43
Isophorone	75	33	77	42
Naphthalene	67	32	75	35
Nitrobenzene	72	31	82	54
N-Nitrosodi-n-propylamine	68	39	76	45
N-Nitrosodiphenylamine	84	24	86	31
PCB-1221	77	11	--	--
PCB-1254	80	13	--	--
Phenanthrene	84	14	76	22
Pyrene	86	15	80	23
1,2,4-Trichlorobenzene	64	16	69	26

Spiked between 5 and 2400 µg/l.

TABLE 5. ACCURACY AND PRECISION FOR ACID EXTRACTABLES

Parameter	Reagent water		Wastewater	
	Average percent recovery	Standard deviation (%)	Average percent recovery	Standard deviation (%)
4-Chloro-3-methylphenol	79	18	75	21
2-Chlorophenol	70	23	71	25
2,4-Dichlorophenol	74	24	80	21
2,4-Dimethylphenol	64	25	58	26
2,4-Dinitrophenol	78	21	108	56
2-Methyl-4,6-dinitrophenol	83	18	90	35
4-Nitrophenol	41	20	43	16
2-Nitrophenol	75	25	75	27
Pentachlorophenol	86	20	66	36
Phenol	36	14	36	21
2,4,6-Trichlorophenol	77	20	81	20

Spikes ranged from 10 to 1500 µg/l.

## METHOD 8270

### GC/MS METHOD FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

#### 1.0 Scope and Application

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in a variety of solid waste matrices.

1.2 This method is applicable to nearly all types of samples, regardless of water content, including aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.3 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

1.4 The detection limit of Method 8270 for determining an individual compound is approximately 1 µg/g (wet weight). For samples that contain more than 1 mg/g of total solvent extractable material, the detection limit is proportionately higher.

1.5 Method 8270 is based upon a solvent extraction, gas chromatographic/mass spectrometric (GC/MS) procedure.

1.6 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

#### 2.0 Summary of Method

2.1 Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method - i.e., separatory funnel liquid-liquid extraction (Method 3510), sonication (Method 3550), or soxhlet extraction (Method 3540). If emulsions are a problem, continuous extraction techniques should be used. This method describes chromatographic conditions which allow for the separation of the compounds in the extract.

### 3.0 Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All 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 waste being sampled.

3.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. Heating in a muffle furnace at 450° C for 5 to 15 hr is recommended whenever feasible. Alternatively, detergent washes, water rinses, acetone rinses, and oven drying may be used. Cleaned glassware should be sealed and stored in a clean environment to prevent any accumulation of dust or other contaminants.

3.2.2 The use of high purity reagents and solvents helps to minimize interference problems.

### 4.0 Apparatus

4.1 Sampling equipment: Glass screw-cap vials or jars of at least 100-ml capacity. Screw caps must be Teflon lined.

#### 4.2 Glassware

4.2.1 Beaker: 400-ml.

4.2.2 Centrifuge tubes: approximately 200-ml capacity, glass with screw cap (Corning #1261 or equivalent). Screw caps must be fitted with Teflon liners.

4.2.3 Concentrator tube, Kuderna-Danish: 25-ml, graduated (Kontes K 570050-2526 or equivalent). Calibration must be checked at the volumes employed in the test. Ground-glass stopper is used to prevent evaporation of extracts.

4.2.4 Evaporative flask: Kuderna-Danish 250-ml (Kontes K-570001-0250 or equivalent). Attach to concentrator tube with springs.

4.2.5 Snyder column, Kuderna-Danish: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.2.6 Snyder column, Kuderna-Danish: Two-ball micro (Kontes K-569001-0219 or equivalent).

#### 4.3 Filter assembly

4.3.1 Syringe: 10-ml gas-tight with Teflon luer lock (Hamilton 1010TLL or equivalent).

4.3.2 Filter holder: 13-mm Swinny (Millipore XX30-012 or equivalent)

4.3.3 Prefilters: glass fiber (Millipore AP-20-010 or equivalent).

4.3.4 Membrane filter: 0.2- $\mu$ m Teflon (Millipore FGLP-013 or equivalent)

4.4 Micro syringe: 100- $\mu$ l (Hamilton #84858 or equivalent).

4.5 Weighing pans, micro: approximately 1-cm diameter aluminum foil. Purchase or fabricate from aluminum foil.

4.6 Boiling chips: Approximately 10-40 mesh carborundum (A.H. Thomas #1590-D30 or equivalent). Heat to 450° C for 5-10 hr or extract with methylene chloride.

4.7 Water bath: Heated, capable of temperature control ( $\pm 2^\circ$  C). The bath should be used in a hood.

4.8 Balance: Analytical, capable of accurately weighing 0.0001 g.

4.9 Microbalance: Capable of accurately weighing to 0.001 mg (Mettler model ME-30 or equivalent).

4.10 Homogenizer, high speed: Brinkmann Polytron model PT 10ST with Teflon bearings, or equivalent.

4.11 Centrifuge: Capable of accommodating 200-ml glass centrifuge tubes.

4.12 pH Meter and electrodes: Capable of accurately measuring pH to  $\pm 0.1$  pH unit.

4.13 Spatula: Having a metal blade 1-2 cm in width.

4.14 Heat lamp: 250-watt reflector-type bulb (GE #250R-40/4 or equivalent) in a heat-resistant fixture whose height above the sample may be conveniently adjusted.

#### 4 / ORGANIC ANALYTICAL METHODS - GC/MS

##### 4.15 Gas chromatograph/mass spectrometer data system

4.15.1 Gas chromatograph: An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories including syringes, analytical columns, and gases.

4.15.2 Column: 30-m x 0.25-mm bonded-phase silicone-coated fused silica capillary column (J&W Scientific DB-5 or equivalent).

4.15.3 Mass spectrometer: Capable of scanning from 35 to 450 amu every 1 sec or less, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode and producing a mass spectrum which meets all the criteria in Table 1 when 50 ng of decafluorotriphenylphosphine (DFTPP) is injected through the GC inlet.

TABLE 1. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA<sup>a</sup>

Mass	Ion abundance criteria
51	30-60% of mass 198
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197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	Greater than 1% of mass 198
441	Present but less than mass 443
442	Greater than 40% of mass 198
443	17-23% of mass 442

<sup>a</sup>J.W. Eichelberger, L.E. Harris, and W.L. Budde. 1975. Reference compound to calibrate ion abundance measurement in gas chromatography-mass spectrometry. Analytical Chemistry 47:995.

4.15.4 GC/MS interface: Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria (see Sections 7.2.1-7.2.4) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. The interface must be capable of transporting at least 10 ng of the components of interest from the GC to the MS. The fused silica column may also be inserted directly into the MS source housing.

4.15.5 Data system: A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundance in any EICP between specified time or scan number limits.

#### 4.16 Gel permeation chromatography system

4.16.1 Chromatographic column: 600-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.16.2 Bio-beads S-X8: 80 g per column.

4.16.3 Pump: Capable of constant flow of 0.1 to 5 ml/min at up to 100 psi.

4.16.4 Injector: With 5-ml loop.

4.16.5 Ultraviolet detector: 254 nm.

4.16.6 Strip chart recorder.

### 5.0 Reagents

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each compound of interest.

5.2 Potassium phosphate, tribasic ( $K_3PO_4$ ): Granular (ACS).

5.3 Phosphoric acid ( $H_3PO_4$ ): 85% aqueous solution (ACS).

5.4 Sodium sulfate, anhydrous ( $Na_2SO_4$ ): Powder (ACS).

## 6 / ORGANIC ANALYTICAL METHODS - GC/MS

5.5 Methylene chloride: Distilled-in-glass quality (Burdick and Jackson, or equivalent).

5.6 D<sub>10</sub>-Phenanthrene.

5.7 Decafluorotriphenylphosphine (DFTPP).

5.8 Retention time standards: D<sub>3</sub>-phenol, D<sub>8</sub>-naphthalene, D<sub>10</sub>-phenanthrene, D<sub>12</sub>-chrysene, and D<sub>12</sub>-benzo(a)pyrene. D<sub>12</sub>-perylene may be used in place of D<sub>12</sub>-benzo(a)pyrene.

5.9 Column performance standards: D<sub>3</sub>-phenol, D<sub>5</sub>-aniline, D<sub>5</sub>-nitrobenzene, and D<sub>3</sub>-2,4-dinitrophenol.

5.10 Surrogate standards: Decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol.

5.11 GPC calibration solution: Methylene chloride containing 100 mg corn oil, 20 mg di-n-octyl phthalate, 3 mg coronene, and 2 mg sulfur per 100 ml.

### 6.0 Sample Collection, Preservation, and Handling

6.1 Grab samples must be collected in glass containers having Teflon-lined screw caps. Sampling equipment must be free of oil and other potential sources of contamination.

6.2 The samples must be iced or refrigerated at 4° C from the time of collection until extraction.

6.3 All samples must be extracted within 14 days of collection and completely analyzed within 40 days of extraction.

### 7.0 Procedure

#### 7.1 Calibration

7.1.1 An internal standard calibration procedure is used. To use this approach, the analyst must use D<sub>3</sub>-phenol, D<sub>8</sub>-naphthalene, D<sub>10</sub>-phenanthrene, D<sub>12</sub>-chrysene and D<sub>12</sub>-benzo(a)pyrene. D<sub>12</sub>-perylene may be substituted for D<sub>12</sub>benzo(a)pyrene. The analyst must further demonstrate that measurement of the internal standard is not affected by method or matrix interferences. Use the base peak ion as the primary ion for quantification of the standards. If interferences are noted, use the next most intense ion as the secondary ion. The internal standard is added to all calibration standards and all sample extracts analyzed by GC/MS. Retention time standards, column performance standards,

and a mass spectrometer tuning standard may be included in the internal standard solution used.

7.1.1.1 A set of five or more retention time standards is selected that will permit all components of interest in a chromatogram to have retention times of 0.85 to 1.20 relative to at least one of the retention time standards. The retention time standards should be similar in analytical behavior to the compounds of interest and their measurement should not be affected by method or matrix interferences. The following retention time standards are recommended for general use: D<sub>3</sub>-phenol, D<sub>8</sub>-naphthalene, D<sub>12</sub>-chrysene, and D<sub>12</sub>-benzo(a)pyrene. D<sub>12</sub>-perylene may be substituted for D<sub>12</sub>-benzo(a)pyrene. D<sub>10</sub>-phenanthrene serves as a retention time standard as well as an internal standard.

7.1.1.2 Representative acidic, basic, and polar neutral compounds are added with the internal standard to assess the column performance of the GC/MS system. The measurement of the column performance standards should not be affected by method or matrix interferences. The following column performance standards are recommended for general use: D<sub>5</sub>-phenol or D<sub>3</sub>-phenol, D<sub>5</sub>-aniline, D<sub>5</sub>-nitrobenzene, and D<sub>3</sub>-2,4-dinitrophenol. These compounds can also serve as retention time standards if appropriate and the retention time standards recommended in Section 7.1.1.1 can serve as column performance standards if appropriate.

7.1.1.3 Decafluorotriphenylphosphine (DFTPP) is added to the internal standard solution to permit the mass spectrometer tuning for each GC/MS run to be checked.

7.1.1.4 Prepare the internal standard solution by dissolving, in 50.0 ml of methylene chloride, 10.0 mg of each standard compound specified in Sections 7.1.1.1, 7.1.1.2, and 7.1.1.3. The resulting solution will contain each standard at a concentration of 200 µg/ml.

7.1.2 Prepare calibration standards at a minimum of three concentration levels for each compound of interest. Each ml of each calibration standard or standard mixture should be mixed with 250 µl of the internal standard solution. One of the calibration standards should be at a concentration near, but above, the method detection limit, 1 to 10 µg/ml, and the other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC/MS system.

7.1.3 Analyze 1 µl of each calibration standard and tabulate the area of the primary characteristic ion against concentration for each compound including standard compound. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

$A_S$  = Response for the parameter to be measured.

$A_{IS}$  = Response for the internal standards.

$C_{IS}$  = Concentration of the internal standard in  $\mu\text{g/l}$ .

$C_S$  = Concentration of the compound to be measured in  $\mu\text{g/l}$ .

If the RF value over the working range is constant (less than 20% relative standard deviation), the RF can be assumed to be invariant and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios,  $A_S/A_{IS}$ , against RF.

7.1.4 The RF must be verified on each working day by the measurement of two or more calibration standards, including one at the beginning of the day and one at the end of the day. The response factors obtained for the calibration standards analyzed immediately before and after a set of samples must be within  $\pm 20\%$  of the response factor used for quantification of the sample concentrations.

## 7.2 Daily GC/MS performance tests

7.2.1 At the beginning of each day that analyses are to be performed, the GC/MS system must be checked to see that acceptable performance criteria are achieved for DFTPP.

7.2.2 The DFTPP performance test requires the following instrumental parameters:

Electron energy: 70 volts (nominal)

Mass Range: 40 to 450 amu

Maximum Scan Time: 1 sec per scan

7.2.3 Inject a solution containing 50  $\mu\text{g/ml}$  of DFTPP into the GC/MS system or bleed DFTPP vapor directly into the mass spectrometer and tune the instrument to achieve all the key ion criteria for the mass spectrum of DFTPP given in Table 1.

7.2.4 DFTPP is included in the internal standard solution added to all samples and calibration solutions. If any key ion abundance observed for DFTPP during the analysis of a sample differs by more than 10% absolute abundance from that observed during the analysis of the

calibration solution, then the analysis in question is considered invalid. The instrument must be retuned or the sample and/or calibration solution reanalyzed until the above condition is met.

### 7.3 Sample extraction

7.3.1 Samples may be extracted by Methods 3510, 3540, or 3550, or by the following procedure. The extraction procedure involves homogenization of the sample with methylene chloride, neutralization to pH 7, and the addition of anhydrous sodium sulfate to remove the water. The amount of acid or base required for the neutralization is determined by titration of the sample. Aqueous samples are extracted using Method 3510 while organic liquids may be analyzed neat or diluted with  $\text{CH}_2\text{Cl}_2$  and analyzed. Solids and semisolids are extracted by Methods 3540 and 3550 or by the extraction described in Steps 7.3.1 through 7.3.3.

7.3.1.1 Thoroughly mix the sample to enable a representative sample to be obtained. Weigh 3.0 g (wet weight) of sample into a 400-ml beaker. Add 75 ml methylene chloride and 150 ml water.

7.3.1.2 Homogenize the mixture for a total of 1 min using a high-speed homogenizer. Use a metal spatula to dislodge any material that adheres to the beaker or to the homogenizer before or during the homogenization to ensure thorough dispersion of the sample.

7.3.1.3 Adjust the pH of the mixture to  $7.0 \pm 0.2$  by titration with 0.4 M  $\text{H}_3\text{PO}_4$  or 0.4 M  $\text{K}_3\text{PO}_4$  using a pH meter to measure the pH. Record the volume of acid or base required.

7.3.2 The extraction with methylene chloride is performed using a fresh portion of the sample. Weigh 3.0 g (wet weight) of sample into a 200-ml centrifuge tube. Spike the sample with surrogate standards as described in Section 8.4. Add 150 ml of methylene chloride followed by 1.0 ml of 4 M phosphate buffer pH 7.0, and an amount of 4 M  $\text{H}_3\text{PO}_4$  or 4 M  $\text{K}_3\text{PO}_4$  equal to one tenth of the pH 7 acid or base volume requirement determined in Section 7.3.1.3. For example, if the acid requirement in Section 7.3.1.3 was 2.0 ml of 0.4 M  $\text{H}_3\text{PO}_4$ , the amount of 4 M  $\text{H}_3\text{PO}_4$  needed would be 0.2 ml.

7.3.3 Homogenize the mixture for a total of 30 sec using a high-speed homogenizer at full speed. Cool the mixture in an ice bath or cold water bath, if necessary, to maintain a temperature of 20-30° C. Use a metal spatula to help dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization to obtain as thorough a dispersion of the sample as possible. Some samples, especially those that contain much water, may not disperse well in this step but will disperse after sodium sulfate is added. Add an amount of anhydrous sodium sulfate powder equal to 15.0 g plus 3.0 g per ml of the 4 M  $\text{H}_3\text{PO}_4$  or 4 M  $\text{K}_3\text{PO}_4$  added in Section 7.3.2. Homogenize the mixture again for a total of 30 sec using a high-speed homogenizer at full speed. Use a metal spatula to dislodge any material that adheres to the centrifuge tube or homogenizer during the homogenization

to ensure thorough dispersion. (NOTE: This step may cause rapid deterioration of the Teflon bearing in the homogenizer. The bearing must be replaced whenever the rotor shaft becomes loose to prevent damage to stainless steel parts.) Allow the mixture to stand until a clear supernatant is obtained. Centrifuge if necessary to facilitate the phase separation. Filter the supernatant required for Sections 7.3.4, 7.3.5, and 7.3.7 (at least 2 ml) through a 0.2- $\mu$ m Teflon filter.

7.3.4 Estimate the total solvent extractable content (TSEC) of the sample by determining the residue weight of an aliquot of the supernatant from Section 7.3.3. Transfer 0.1 ml of the supernatant to a tared aluminum weighing dish, place the weighing dish under a heat lamp at a distance of 8 cm from the lamp for 1 min to allow the solvent to evaporate, and weigh on a microbalance. If the residue weight of the 0.1-ml aliquot is less than 0.05 mg, concentrate 25 ml of the supernatant to 1.0 ml and obtain a residue weight on 0.1 ml of the concentrate. For the concentration step, use a 25-ml evaporator tube fitted with a micro Snyder column; add two boiling chips and heat in a water bath at 60-65° C. Calculate the TSEC as milligrams of residue per gram of sample using Equation 1 if concentration was not required or Equation 2 if concentration was required.

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of supernatant}}{0.002} \quad (\text{Eq. 1})$$

$$\frac{\text{mg of residue}}{\text{g of sample}} = \frac{\text{residue weight (mg) of 0.1 ml of conc. supernatant}}{0.05} \quad (\text{Eq. 2})$$

7.3.5 If the TSEC of the sample (as determined in Section 7.3) is less than 50 mg/g, concentrate an aliquot of the supernatant that contains a total of only 10 to 20 mg of residual material. For example, if the TSEC is 44 mg/g, use a 20-ml aliquot of the supernatant, which will contain 17.6 mg of residual material, or if the TSEC is 16 mg/g, use a 50-ml aliquot of the supernatant, which will contain 16.0 mg of residual material. If the TSEC is less than 10 mg/g, use 100 ml of the supernatant. Perform the concentration by transferring the aliquot of the supernatant to a K-D flask fitted into a 25-ml concentrator tube. Add two boiling chips, attach a three-ball macro Snyder column to the K-D flask, and concentrate the extract using a water bath at 60 to 65° C. Place the K-D apparatus in the water bath so that the concentrator tube is about half immersed in the water and the entire 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 min. 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 of 5 to 6 ml, remove the K-D apparatus from the water bath and allow the solvent to drain for at least 5 min while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with the methylene

chloride to bring the volume to 10.0 ml. Mix the contents of the concentrator tube by inserting a stopper and inverting several times.

7.3.6 Analyze the concentrate from Section 7.3.5 or, if the TSEC of the sample is 50 mg/g or more, analyze the supernatant from Section 7.3 using gas chromatography. Use a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column under the chromatographic conditions described in Section 7.5. Estimate the concentration factor or dilution factor required to give the optimum concentration for the subsequent GC/MS analysis. In general, the optimum concentration will be one in which the average peak height of the five largest peaks or the height of an unresolved envelope of peaks is the same as that of an internal standard at a concentration of 50-100 µg/ml.

7.3.7 If the optimum concentration determined in Section 7.3.6 is 20 mg of residual material per ml or less, proceed to Section 7.3.8. If the optimum concentration is greater than 20 mg of residual material per ml and if the TSEC is greater than 50 mg/g, apply the GPC cleanup procedure described in Section 7.4. For the GPC cleanup, concentrate 90 ml of the supernatant from Section 7.3.3 or a portion of the supernatant that contains a total of 600 mg of residual material (whichever is the smaller volume). Use the concentration procedure described in Section 7.3.5 and concentrate to a final volume of 15.0 ml. Stop the concentration prior to reaching 15.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume equal to the volume of supernatant used) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out.)

7.3.8 Concentrate further or dilute as necessary an aliquot of the concentrate from Section 7.3.5 or an aliquot of the supernatant from Section 7.3.3, or if GPC cleanup was necessary, an aliquot of the concentrate from Section 7.4.3 to obtain 1.0 ml of a solution having the optimum concentration, as described in Section 7.3.6, for the GC/MS analysis. If the aliquot needs to be diluted, dilute it to a volume of 1.0 ml with methylene chloride. If the aliquot needs to be concentrated, concentrate it to 1.0 ml as described in Section 7.3.4. Do not let the volume in the concentrator tube go below 0.6 ml at any time. Stop the concentration prior to reaching 1.0 ml if any oily or semisolid material separates out and dilute as necessary (up to a maximum final volume of 10 ml) to redissolve the material. (Disregard the presence of small amounts of inorganic salts that may settle out). Add 250 µl of the internal standard solution, containing 50 µg each of the internal standard, retention time standards, column performance standards, and DFTPP, to 1.0 ml of the final concentrate and save for GC/MS analysis as described in Section 7.5. Calculate the concentration in the original sample that is represented by the internal standard using Equation 3 if an aliquot of the concentrate from Section 7.3.5 was used in Section 7.3.8, Equation 4 if an aliquot of the supernatant from Section 7.3.3

was used in Section 7.3.8 or Equation 5 if an aliquot of the GPC concentrate from Section 7.4.3 was used in Section 7.3.8.

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.5)}} \times \frac{10}{V_{c(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 3})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.8)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 4})$$

$$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}} = \frac{50}{3} \times \frac{150}{V_{s(7.3.7)}} \times \frac{V_F}{V_{\text{GPC}(7.3.7)}} \times \frac{\text{Final Vol. (ml)}}{1} \quad (\text{Eq. 5})$$

where:

$V_s$  = Volume of supernatant from Section 7.3.3 used in Sections 7.3.5, 7.3.8, 7.3.7

$V_{c(7.3.8)}$  = Volume of concentrate from Section 7.3.5 used in Section 7.3.8

$V_F(7.3.7)$  = Final volume of concentrate in Section 7.3.7

$V_{\text{GPC}}$  = Volume of GPC concentrate from Section 7.4.3 used in Section 7.3.8

Use this calculated value for the quantification of individual compounds as described in Section 7.7.2.

#### 7.4 Cleanup using gel permeation chromatography

7.4.1 Prepare a 600-mm x 25-mm I.D. gel permeation chromatography (GPC) column by slurry packing using 80 g of Bio-Beads S-X8 that have been swelled in methylene chloride for at least 4 hr. Prior to initial use, rinse the column with methylene chloride at 1 ml/min for 16 hr to remove any traces of contaminants. Calibrate the system by injecting 5 ml of the GPC calibration solution, eluting with methylene chloride at 5 ml/min for 50 min and observing the resultant UV detector trace. The column may be used indefinitely as long as no darkening or pressure increases occur and a column efficiency of at least 500 theoretical plates is achieved. The pressure should not be permitted to exceed 50 psi. Recalibrate the system daily.

7.4.2 Inject a 5-ml aliquot of the concentrate from Section 7.3.7 onto the GPC column and elute with methylene chloride at 5 ml/min for 50 min. Discard the first fraction that elutes up to a retention time represented by the minimum between the corn oil peak and the di-n-octyl

phthalate peak in the calibration run. Collect the next fraction eluting up to a retention time represented by the minimum between the coronene peak and the sulfur peak in the calibration run. Apply the above GPC separation to a second 5-ml aliquot of the concentrate from Section 7.3.7 and combine the fractions collected.

7.4.3 Concentrate the combined GPC fractions to 10.0 ml as described in Section 7.3.5. Estimate the TSEC of the concentrate as described in Section 7.3.4. Estimate the TSVc of the concentrate as described in Section 7.3.6.

## 7.5 Gas chromatography/mass spectrometry

7.5.1 Analyze the 1-ml concentrate from Section 7.3.8 by GC/MS using a 30-m x 0.25-mm bonded-phase silicone-coated fused-silica capillary column. The recommended GC operating conditions to be used are as follows:

Initial column temperature hold: 40° C for 4 min

Column temperature program: 40-270° C at 10 degrees/min

Final column temperature hold: 270° C (until Benzo(ghi)perylene has eluted)

Injector temperature: 290° C

Transfer line temperature: 300° C

Injector: Grob-type, splitless

Sample volume: 1-2 µl

Carrier gas: Hydrogen (preferred) at 50 cm/sec or helium at 30 cm/sec

7.5.2 If the response for any ion exceeds the working range of the GC/MS system, dilute the extract and reanalyze.

7.5.3 Perform all qualitative and quantitative measurements as described in Sections 7.6 and 7.7. When the extracts are not being used for analyses, store them at 4° C protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

## 7.6 Qualitative identification

7.6.1 Obtain an EICP for the primary characteristic ion and at least two other characteristic ions for each compound when practical. The following criteria must be met to make a qualitative identification.

7.6.1.1 The characteristic ions for each compound of interest must maximize in the same or within one scan of each other.

7.6.1.2 The retention time must fall within  $\pm 15$  sec (based on the relative retention time) of the retention time of the authentic compound.

7.6.1.3 The relative peak heights of the characteristic ions in the EICP's must fall within  $\pm 20\%$  of the relative intensities of these ions in a reference mass spectrum.

## 7.7 Quantitative determination

7.7.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. In general, the primary characteristic ion selected should be a relatively intense ion as interference-free as possible, and as close as possible in mass to the characteristic ion of the internal standard used.

7.7.2 Use the internal standard technique for performing the quantification. Calculate the concentration of each individual compound of interest in the sample using Equation 6.

$$\text{Concentration, } \mu\text{g/g} = \frac{\mu\text{g of Int. Std.}}{\text{g of sample}} \times \frac{A_S}{A_{IS}} \times \frac{1}{\text{RF}} \quad (\text{Eq. 6})$$

where:

$\frac{\mu\text{g of Int. Std.}}{\text{g of sample}}$  = internal standard concentration factor calculated in Section 7.3.8.

$A_S$  = Area of the primary characteristic ion of the compound being quantified

$A_{IS}$  = Area of the primary characteristic ion of the internal standard

RF = Response factor of the compound being quantified (determined in Section 7.1.3).

7.7.3 Report results in  $\mu\text{g/g}$  without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.7.4 If the surrogate standard recovery falls outside the control limits in Section 8.3, the data for all compounds in that sample must be labeled as suspect.

## 8.0 Quality Control

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within the accuracy and precision limits expected of the method.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 The laboratory must spike all samples including check samples with surrogate standards to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations using a representative sample as a check sample.

8.2.1 Analyze four aliquots of the unspiked check sample according to the method beginning in Section 7.3.

8.2.2 For each compound to be measured, select a spike concentration representative of twice the level found in the unspiked check sample or a level equal to 10 times the expected detection limit, whichever is greater. Prepare a spiking solution by dissolving the compounds in methylene chloride at the appropriate levels.

8.2.3 Spike a minimum of four aliquots of the check sample with the spiking solution to achieve the selected spike concentrations. Spike the samples after they have been transferred to centrifuge tubes for extraction. Analyze the spiked aliquots according to the method described beginning in Section 7.3.

8.2.4 Calculate the average percent recovery ( $R$ ) and the standard deviation of the percent recovery ( $s$ ) for all compounds and surrogate standards. Background corrections must be made before  $R$  and  $s$  calculations are performed. The average percent recovery must be greater than 20 for all compounds to be measured and greater than 60 for all surrogate compounds. The percent relative standard deviation of the percent recovery ( $s/R \times 100$ ) must be less than 20 for all compounds to be measured and all surrogate compounds.

8.3 The analyst must calculate method performance criteria for each of the surrogate standards.

8.3.1 Calculate upper and lower control limits for method performance for each surrogate standard, using the values for R and s calculated in Section 8.2.4:

$$\text{Upper Control Limit (UCL)} = R + 3s$$

$$\text{Lower Control Limit (LCL)} = R - 3s$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

8.3.2 For each surrogate standard, the laboratory must maintain a record of the R and s values obtained for each surrogate standard in each waste sample analyzed. An accuracy statement should be prepared from these data and updated regularly.

8.4 The laboratory is required to spike all samples with the surrogate standard to monitor spike recoveries. The spiking level used should be that which will give a concentration in the final extract used for GC/MS analysis that is equal to the concentration of the internal standard assuming a 100% recovery of the surrogate standards. For unknown samples, the spiking level is determined by performing the extraction steps in Section 7.3 on a separate aliquot of the sample and calculating the amount of internal standard per gram of sample as described in Section 7.3.8. If the recovery for any surrogate standard does not fall within the control limits for method performance, the results reported for that sample must be qualified as being outside of control limits. The laboratory must monitor the frequency of data so qualified to ensure that it remains at or below 5%. Three surrogate standards, namely decafluorobiphenyl, 2-fluoroaniline, and pentafluorophenol, are recommended for general use to monitor recovery of neutral, basic, and acidic compounds, respectively.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a process blank that all glassware and reagent interferences are under control. Each time a set of samples is extracted or there is a change in reagents, a process blank should be analyzed to determine the level of laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field replicates may be analyzed to monitor the precision of the sample technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

8.7 The features that must be monitored for each GC/MS analysis run for quality control purposes and for which performance criteria must be met are as follows:

- Relative ion abundances of the mass spectrometer tuning compound DFTPP.
- Response factors of column performance standards and retention time standards.
- Relative retention time of column performance standards and retention time standards.
- Peak area intensity of the internal standard, e.g., D<sub>10</sub>-phenanthrene.

### 8.3 High Performance Liquid Chromatographic Methods (8300's)

Methods appropriate for organic analysis by HPLC methods are included on the following pages.

## METHOD 8310

### POLYNUCLEAR AROMATIC HYDROCARBONS

#### 1.0 Scope and Application

Method 8310 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in groundwater and wastes. Specifically, Method 8310 is used to detect the following substances:

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(ghi)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

1.2 Use of Method 8310 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 detection limits for Method 8310 are listed in Table 1. The sensitivity of this method usually depends on the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

#### 2.0 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. The compounds in the extract are then measured by High Performance Liquid Chromatography (HPLC).

2.2 A general purpose cleanup procedure to aid the analyst in eliminating interferences is described.

#### 3.0 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 these materials must be demonstrated to be free from interferences under the conditions of the analysis by running

TABLE 1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PAH<sup>a</sup>

Compound	Retention time (min)	Detection limit ( $\mu\text{g/l}$ )	
		UV	Fluorescence
Naphthalene	16.17	1.8	
Acenaphthylene	18.10	2.3	
Acenaphthene	20.14	1.8	
Fluorene	20.89	0.21	
Phenanthrene	22.32		0.64
Anthracene	23.78		0.66
Fluoranthrene	25.00		0.21
Pyrene	25.94		0.27
Benzo(a)anthracene	29.26		0.013
Chrysene	30.14		0.15
Benzo(b)fluoranthene	32.44		0.018
Benzo(k)fluoranthene	33.91		0.017
Benzo(a)pyrene	34.95		0.023
Dibenzo(a,h)anthracene	37.06		0.030
Benzo(ghi)perylene	37.82		0.076
Indeno(1,2,3-cd)pyrene	39.21		0.043

<sup>a</sup>HPLC conditions: Reverse phase HC-ODS Sil-X 2.6 x 250 mm Perkin-Elmer column; isocratic elution for 5 min using 40% acetonitrile/60% water, then linear gradient elution to 100% acetonitrile over 25 min; flow rate is 0.5 ml/min.

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 cleanup technique is provided as part of this method, individual samples may require additional cleanup approaches to achieve 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.

3.4 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free. 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 analyses. Where doubt exists over the identification of a peak, confirmatory techniques such as mass spectroscopy should be used.

3.5 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. This is done by spiking each waste sample with known amounts of the compounds that the waste is being analyzed for. Using these spiked waste samples, the sensitivity of the instrument is then readjusted so that 1  $\mu\text{g/g}$  of sample can be readily detected. Detection limits necessary for groundwater monitoring are much lower. The analyst should adjust instrument sensitivity according to Table 1 when analyzing groundwater samples.

#### 4.0 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 / ORGANIC ANALYTICAL METHODS - HPLC

4.2 Separatory funnel: 2000 ml, with Teflon stopcock.

4.3 Drying column: 20-mm-I.D. 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 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 ( $\pm 2^\circ$  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 x 2.6 mm I.D. (Perkin Elmer No. 809-0716 or equivalent).

4.6.3 Fluorescence detector, for excitation at 280 nm and emission at 380 nm.

4.6.4 UV detector, 254 nm, coupled fluorescence detector.

4.6.5 Strip chart recorder compatible with detectors. (A data system for measuring peak areas is recommended.)

4.7 Chromatographic column: 250 mm long x 10 mm I.D. with coarse-fritted disc at bottom and Teflon stopcock.

## 5.0 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  $400^\circ C$  for 4 hr 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 g 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 hr at  $130^\circ C$  in a foil-covered glass container.

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 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.

6.3 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 hr will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hr 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.

6.4 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

## 7.0 Procedure

### 7.1 Sample extraction

7.1.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2-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.

7.1.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 sec to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for 2 min with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the 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.

7.1.3 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.

7.1.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3-4 in. 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.

7.1.5 Add 1 or 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 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 min 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.

7.1.6 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.

7.1.7 If the sample requires cleanup before chromatographic analysis, proceed to Section 7.2. If the sample does not require cleanup, or if the need for cleanup is unknown, analyze an aliquot of the extract according to Section 7.4.

## 7.2 Cleanup and separation

7.2.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1- to 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 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 ml, remove K-D apparatus and allow it to drain for at least 10 min 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.

7.2.2 Prepare a slurry of 10 g activated silica gel in methylene chloride and place this in a 10-mm-I.D. 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.

7.2.3 Preelute the column with 40 ml pentane. Discard the eluate and just prior to exposure to the sodium sulfate layer to the air, transfer the 2-ml cyclohexane sample extract onto the column, using an additional 2 ml cyclohexane to complete the transfer.

7.2.4 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.

7.2.5 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.

7.2.6 Concentrate the collected fraction to less than 10 ml by K-D techniques as in 7.1.5, using pentane to rinse the walls of the glassware. Proceed with HPLC or gas chromatographic analysis.

7.2.7 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.

### 7.3 Calibration

7.3.1 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 1 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.

7.3.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

7.3.3 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.

### 7.4 High Performance Liquid Chromatography (HPLC)

7.4.1 Table 1 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.

7.4.2 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.

7.4.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.4 If the peak area measurement is prevented by the pressure of interference, further cleanup is required.

7.4.5 The UV detector is recommended for the determination of naphthalene and acenaphthylene, and the fluorescence detector is recommended for the remaining PAH.

Column: HC-ODS SIL-X  
Mobile Phase: 40% to 100% Acetonitrile in Water  
Detector: Fluorescence

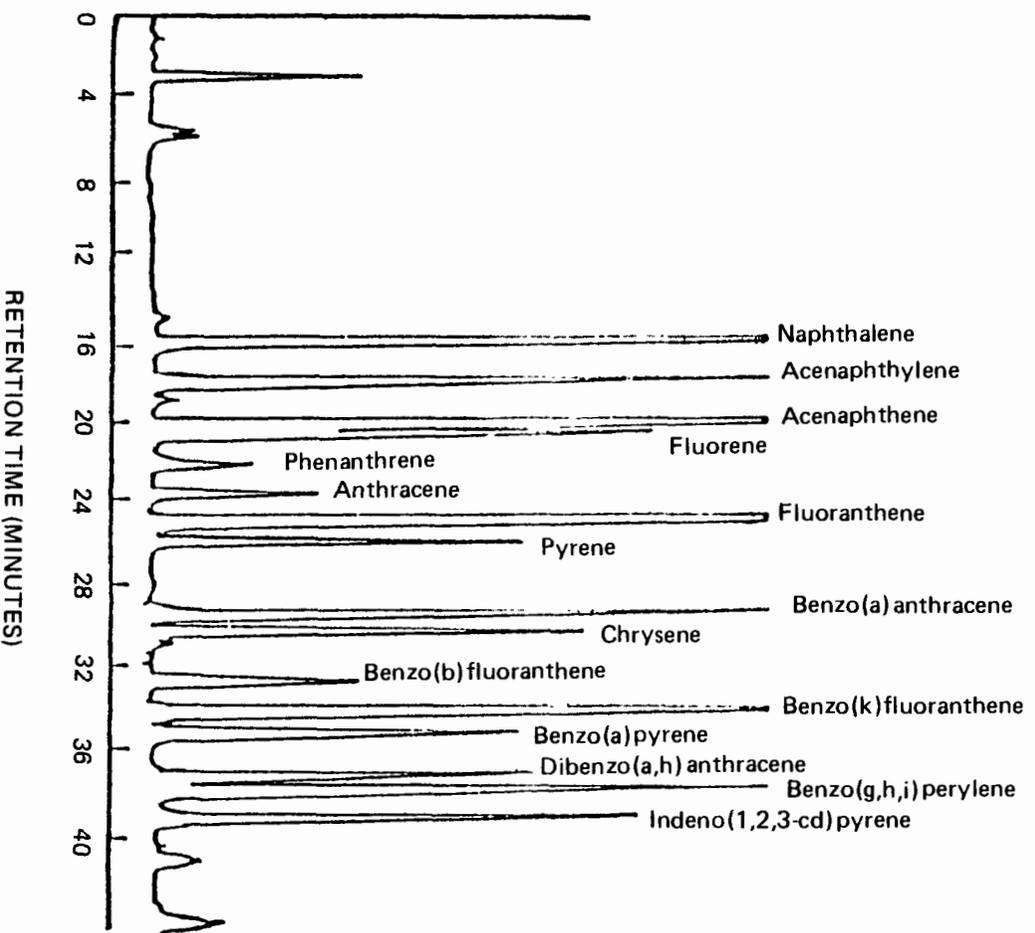


Figure 1. Liquid chromatogram of polynuclear aromatics.

## 7.5 Calculations

7.5.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu\text{g/l} = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

where:

A = Calibration factor for chromatographic system (in ng material per area unit)

B = Peak size in injection of sample extract (in area units)

$V_i$  = Volume of extract injected ( $\mu\text{l}$ )

$V_t$  = Volume of total extract ( $\mu\text{l}$ )

$V_s$  = Volume of water extracted (ml).

7.5.2 Report results in  $\mu\text{g/l}$  without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

## 8.0 Quality Control

8.1 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.

8.2 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 waste samples should be analyzed to validate the accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to  $1 \mu\text{g/g}$  of sample, then the sensitivity of the instrument should be increased or the extract subjected to additional cleanup. Detection limits to be used for groundwater samples are indicated in Table 1. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as fraction collection and GC/MS should be used.

8.3 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

8.4 In a single laboratory, using reagent water and wastewaters spiked at or near background levels, the average recoveries presented in Table 2 were obtained. The standard deviation of the measurement in percent recovery is also included in Table 2.

TABLE 2. SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average percent recovery	Standard deviation percent	Spike range ( $\mu\text{g/l}$ )	Number of analyses	matrix types
Acenaphthene	88	5.7	11.6-25	24	4
Acenaphthylene	93	6.4	250-450	24	4
Anthracene	93	6.3	7.9-11.3	24	4
Benzo(a)anthracene	89	6.9	0.64-0.66	24	4
Benzo(a)pyrene	94	7.4	0.21-0.30	24	4
Benzo(b)fluoranthene	97	12.9	0.24-0.30	24	4
Benzo(ghi)perylene	86	7.3	0.42-3.4	24	4
Benzo(k)fluoranthene	94	9.5	0.14-6.2	24	4
Chrysene	88	9.0	2.0-6.8	24	4
Dibenzo(a,h)anthracene	87	5.8	0.4-1.7	24	4
Fluoranthene	116	9.7	0.3-2.2	24	4
Fluorene	90	7.9	6.1-23	24	4
Indeno(1,2,3-cd)pyrene	94	6.4	0.96-1.4	24	4
Naphthalene	78	8.3	20-70	24	4
Phenanthrene	98	8.4	3.8-5.0	24	4
Pyrene	96	8.5	2.3-6.9	24	4

SECTION NINE

MISCELLANEOUS ANALYTICAL METHODS

Methods appropriate for analysis by a number of miscellaneous analytical methods (9000 series) are included on the following pages.

## METHOD 9010

### TOTAL AND AMENABLE CYANIDE

#### 1.0 Scope and Application

1.1 Method 9010 is used to determine the concentration of inorganic cyanide in a waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9010 does not determine the "reactive" cyanide content of wastes containing iron-cyanide complexes.

#### 2.0 Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCI) by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 570 nm for pyridine-barbituric acid reagent. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

#### 3.0 Interferences

3.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 7.2.3, 7.2.4, and 7.2.5.

3.2 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the optional procedure described in procedure 7.2.3.

3.3. High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid which will react with some organic compounds to form oximes. These compounds formed will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

Revised 4/84

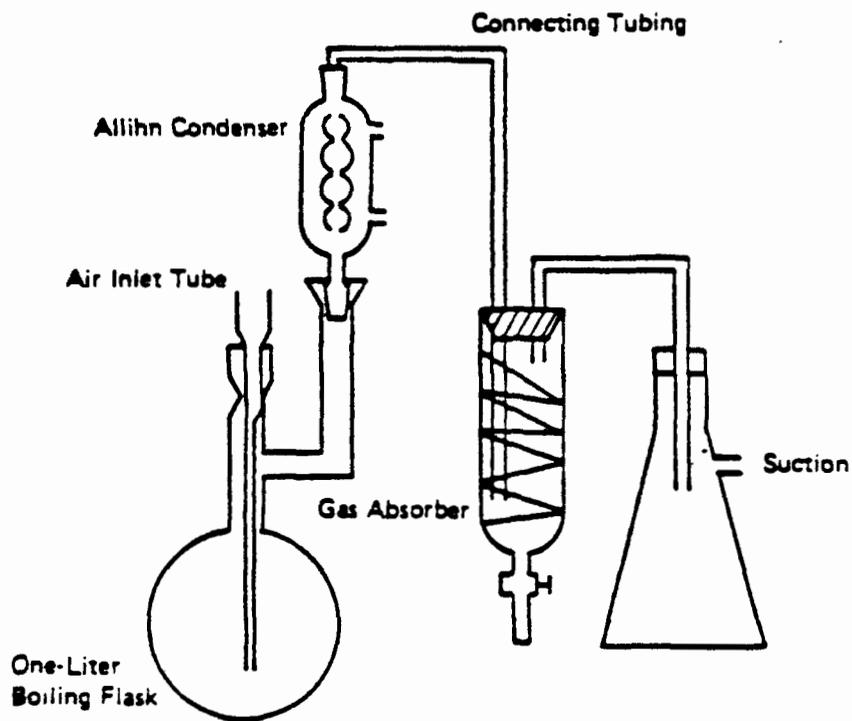


Figure 1. Apparatus for cyanide distillation.

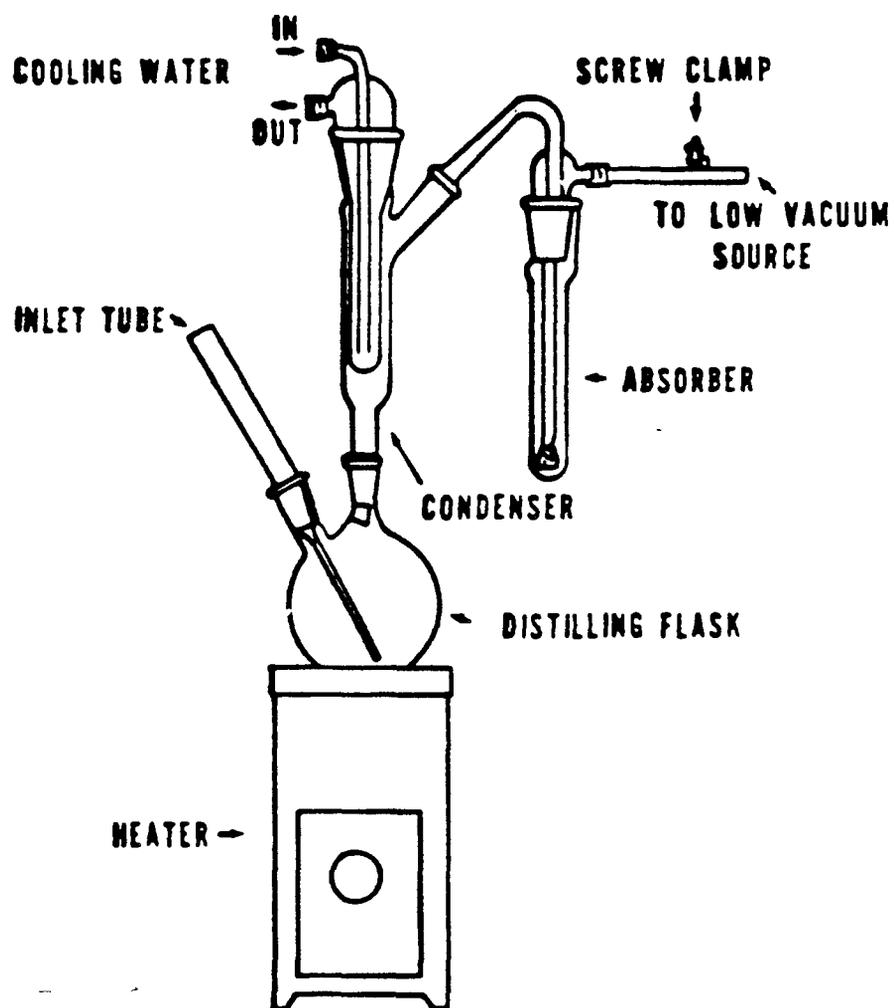


Figure 2. Cyanide distillation apparatus.

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#### 4.0 Apparatus

4.1 Reflux distillation apparatus such as shown in Figure 1 or 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

4.2 Spectrophotometer suitable for measurements at 570 nm with a 1.0 cm cell or larger.

4.3 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

##### 4.4 Technicon Auto-Analyzer

4.4.1 Sampler

4.4.2 Cyanide manifold. (See Figure 3.)

4.4.3 Proportioning pump.

4.4.4 Colorimeter equipped with a 15 mm flowcell and 570 nm filter.

4.4.5 Recorder.

#### 5.0 Reagents

5.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilled water, and dilute to 1 liter with distilled water.

5.2 Bismuth nitrate solution: Dissolve 30.0 grams of  $\text{Bi}(\text{NO}_3)_3$  in 100 mls of distilled water. While stirring, add 250 mls of acetic acid. Stir until dissolved. Dilute to 1 liter with distilled water.

5.3 Sulfuric acid; 18N: Slowly add 500 ml of concentrated  $\text{H}_2\text{SO}_4$  to 500 ml of distilled water.

5.4 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 1 liter of distilled water. Refrigerate this solution.

5.5 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 ml of distilled water. Standardize with 0.0192 N  $\text{AgNO}_3$ . Dilute to appropriate concentration so that 1 ml = 1 mg CN.

5.6 Standard cyanide solution, intermediate: Dilute 100.0 ml of stock (1 ml = 1 mg CN) to 1000 ml with distilled water (1 ml = 100 g).

5.7 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 ml of intermediate cyanide solution to 1000 ml with distilled water and store in a glass stoppered bottle. 1 ml = 10.0 ug CN.

5.8 Magnesium chloride solution: Weigh 510 g of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  into a 1000 ml flask, dissolve and dilute to 1 liter with distilled water.

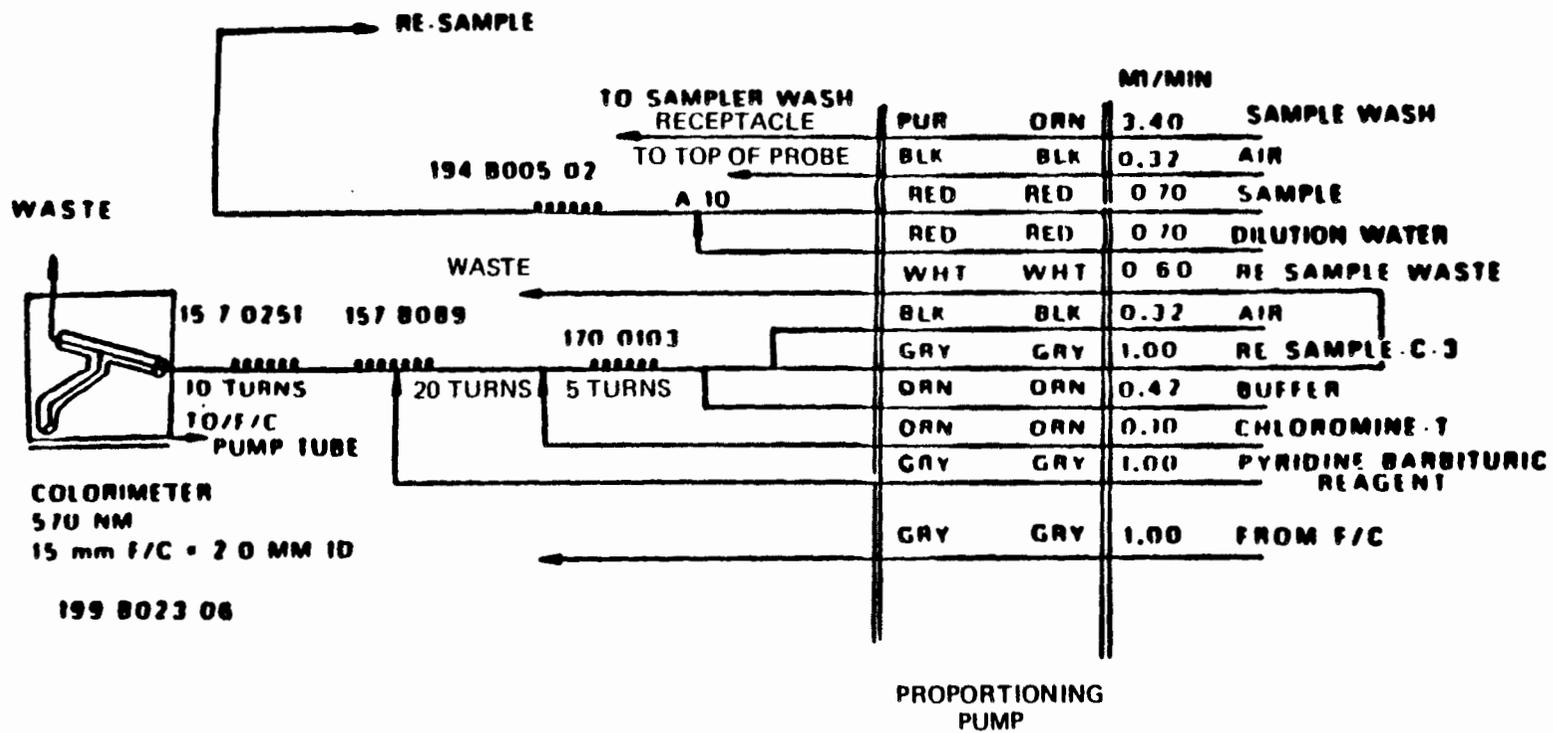


Figure 3. Cyanide manifold AA11.

5.9 Sulfamic acid solution: Dissolve 40 g of sulfamic acid in distilled water. Dilute to 1 liter.

5.10 Calcium Hypochlorite solution: Dissolve 5 g of calcium hypochlorite ( $\text{Ca}(\text{OCl})_2$ ) in 100 ml of distilled water.

5.11 Potassium Iodide-starch test paper.

5.12 Reagents for manual colorimetric determination:

5.12.1 Pyridine-Barbituric Acid Reagent: Place 15 g of barbituric acid in a 250 ml volumetric flask and add just enough distilled water to wash the sides of the flask and wet barbituric acid. Add 75 ml of pyridine and mix. Add 15 ml of conc. HCl, mix and cool to room temperature. Dilute to 250 ml with distilled water and mix., This reagent is stable for approximately six months if stored in a cool, dark place.

5.12.2 Chloramine-T solution: Dissolve 1.0 g of white, water soluble Chloramine-T in 100 ml of distilled water and refrigerate until ready to use.

5.13 Reagents for automated colorimetric determination:

5.13.1 Distillation agent: Carefully add 250 ml of 85% phosphoric acid and 50 ml of hypophosphorus acid to 700 ml of distilled water, mix, and dilute to one liter with distilled water.

5.13.2 Sodium dihydrogenphosphate, 1M (phosphate buffer): Dissolve 138 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  in 1 liter of distilled water. Refrigerate this solution.

5.13.3 Chloramine-T: Dissolve 3.0 g of chloramine-T in 500 ml of distilled water.

5.13.4 Pyradine barbituric acid reagent: Refer to (5.12.1).

5.13.5 Sodium hydroxide, 1 N: Dissolve 40 g of NaOH in 500 ml of distilled water.

5.13.6 Stock cyanide solution: Refer to 5.5.

5.13.7 All working standards should contain 2 ml of 1 N NaOH (5.13.5) per 100 ml.

5.13.8 Dilution water and recepticle wash water (NaOH, 0.25 N): Dissolve 10.0 g NaOH in 500 mls of distilled water. Dilute to 1 liter.

## 6.0 Sample Collection, Preservation and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples should be collected in plastic or glass bottles of 1-liter size or larger. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of water.

6.4 Samples must be preserved with 2 ml of 10 N sodium hydroxide per liter of sample (pH is greater than or equal to 12) at the time of collection.

6.5 Samples should be refrigerated at 4°C when possible and analyzed as soon as possible.

## 7.0 Procedure

### 7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution (5.10) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (5.1).

Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

7.1.2 Test for residual chlorine with KI-starch paper (5.11) and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

7.1.3 After one hour, add 0.5 g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

7.1.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

## 7.2 Distillation Procedure

7.2.1 Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Pipet 50 ml of sodium hydroxide (5.1) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap in the train. (Figure 1 or 2)

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enters the boiling flask through the air inlet tube.

7.2.3 If samples contain sulfide, add 50 ml of bismuth nitrate solution (5.2) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of  $H_2SO_4$ .

7.2.4 If samples contain  $NO_3$  and/or  $NO_2$ , add 50 ml of sulfamic acid solution (5.9) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of  $H_2SO_4$ .

7.2.5 Slowly add 50 ml 18 N sulfuric acid (5.3) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 ml of magnesium chloride (5.8) into the air inlet and wash down with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

7.2.7 Drain the solution from the absorber into a 250 ml volumetric flask. Wash the absorber with distilled water and add the washings to the flask. Dilute to the mark with distilled water.

## 7.3 Manual spectrophotometric determination:

7.3.1 Withdraw 50 ml or less of the solution from the flask and transfer to a 100 ml volumetric flask. If less than 50 ml is taken, dilute to 50 ml with 0.25 N sodium hydroxide solution (5.13.8). Add 15.0 ml of sodium phosphate solution (5.4) and mix.

7.3.2 Add 2 ml of chloramine-T (5.12.2) and mix. See note 1. After 1 to 2 minutes, add 5 ml of pyridine-barbituric acid solution (5.12.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development and then read absorbance at 570 nm in a 1-cm cell within 15 minutes.

#### 7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipeting suitable volumes of standard solution (5.7) into 250 ml volumetric flasks. To each standard add 50 ml of 1.25 N sodium hydroxide and dilute to 250 ml with distilled water. Prepare as follows:

<u>ML of Working Standard Solution</u> <u>(1 ml = 10 g CN)</u>	<u>Conc. g CN</u> <u>per 250 ml</u>
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

7.4.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to insure that the distillation technique is reliable. If distilled standards do not agree within  $\pm 10\%$  of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

7.4.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (5.6) or the working standard (5.7) to 500 ml of sample to insure a level of 20  $\mu\text{g/l}$ . Proceed with the analysis as in Procedure (7.2.1)

#### 7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

7.5.2 Prepare a standard curve by plotting absorbance of standards vs. cyanide concentrations.

7.6 Calculation: If the colormetric procedure is used, calculate the cyanide, in  $\mu\text{g/l}$ , in the original sample as follows:

$$\text{CN, } \mu\text{g/l} = \frac{A \times 1,000}{B} \times \frac{50}{C}$$

where:

A =  $\mu\text{g}$  CN read from standard curve  
B = ml of original sample for distillation  
C = ml taken for colorimetric analysis

#### 7.7 Automated colorimetric determination

7.7.1 Set up the manifold as shown in Figure 3 in a hood or a well ventilated area.

7.7.2 Allow colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding distilled water through the sample line.

7.7.3 Place appropriate standards in the sampler in order of decreasing concentration. Complete loading of sampler tray with unknown samples.

7.7.4 When the baseline becomes steady, begin the analyses.

7.8 Calculation: Prepare standard curve by plotting peak heights of standards against concentration values. Compute concentrations of samples by comparing sample peak heights with standards.

#### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards after approximately every 15 samples.

8.4 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

## METHOD 9020

### TOTAL ORGANIC HALIDES (TOX)

#### 1.0 Scope and Application

1.1 Method 9020 determines Total Organic Halides (TOX) as  $\text{Cl}^-$  in drinking and ground waters. The method uses carbon adsorption with a microcoulometric-titration detector. It requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5  $\mu\text{g}/\text{l}$ .

1.2 Method 9020 detects all organic halides containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine-containing species are not determined by this method.

1.3 Method 9020 is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

1.4 Method 9020 is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcoulometer and in the interpretation of the results.

1.5 This method is provided as a recommended procedure. It may be used as a reference for comparing the suitability of other methods thought to be appropriate for measurement of TOX (i.e., by comparison of sensitivity, accuracy, and precision data).

#### 2.0 Summary of Method

2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and that is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed to remove any trapped inorganic halides, and is then analyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

#### 3.0 Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All these materials must be

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routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400° C for 15 to 30 min. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples that register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

### 4.0 Apparatus and Materials

#### 4.1 Adsorption system

4.1.1 Dohrmann adsorption module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

4.1.2 Adsorption columns: Pyrex, 5-cm-long x 6-mm-O.D. x 2-mm-I.D.

4.2.3 Granular activated carbon (GAC): Filtrasorb-400, Calgon-APC or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000 mg Cl<sup>-</sup> equivalent or less.

4.1.4 Cerafelt (available from Johns-Manville), or equivalent: Form this material into plugs using a 2-mm-I.D. stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

4.1.5 Column holders (available from Dohrmann).

4.1.6 Volumetric flasks: 100-ml, 50-ml. A general schematic of the adsorption system is shown in Figure 1.

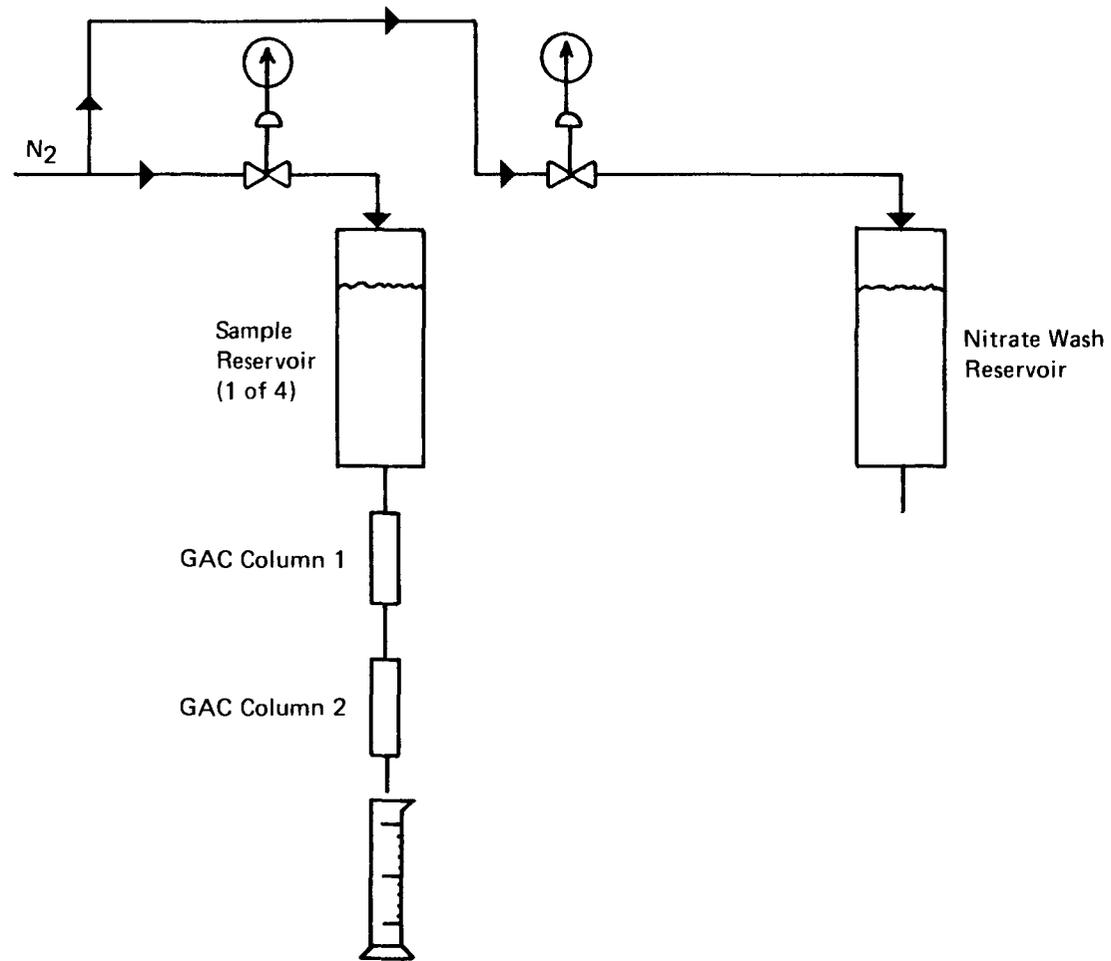


Figure 1. Schematic of Adsorption System.

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4.2 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

4.2.1 Boat sampler.

4.2.2 Pyrolysis furnace.

4.2.3 Microcoulometer with integrator.

4.2.4 Titration cell: A general description of the analytical system is shown in Figure 2.

4.3 Strip chart recorder.

## 5.0 Reagents

5.1 Sodium sulfite: 0.1 M, ACS reagent grade (12.6 g/liter).

5.2 Nitric acid: Concentrated.

5.3 Nitrate-wash solution (5000 mg  $\text{NO}_3^-$ /l): Prepare a nitrate-wash solution by transferring approximately 8.2 g of potassium nitrate into a 1-liter volumetric flask and diluting to volume with reagent water.

5.4 Carbon dioxide: Gas, 99.9% purity.

5.5 Oxygen: 99.9% purity.

5.6 Nitrogen: Prepurified.

5.7 70% acetic acid in water: Dilute 7 volumes of acetic acid with 3 volumes of water.

5.8 Trichlorophenol solution, stock ( $1 \mu\text{l} = 10 \mu\text{g Cl}^-$ ): Prepare a stock solution by weighing accurately 1.856 g of trichlorophenol into a 100-ml volumetric flask. Dilute to volume with methanol.

5.9 Trichlorophenol solution, calibration ( $1 \mu\text{l} = 500 \text{ ng Cl}^-$ ): Dilute 5 ml of the trichlorophenol stock solution to 100 ml with methanol.

5.10 Trichlorophenol standard, instrument-calibration: First, nitrate-wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with  $10 \mu\text{l}$  of the calibration solution.

5.11 Trichlorophenol standard, adsorption-efficiency ( $100 \mu\text{g Cl}^-$ /liter): Prepare an adsorption-efficiency standard by injecting  $10 \mu\text{l}$  of stock solution into 1 liter of reagent water.

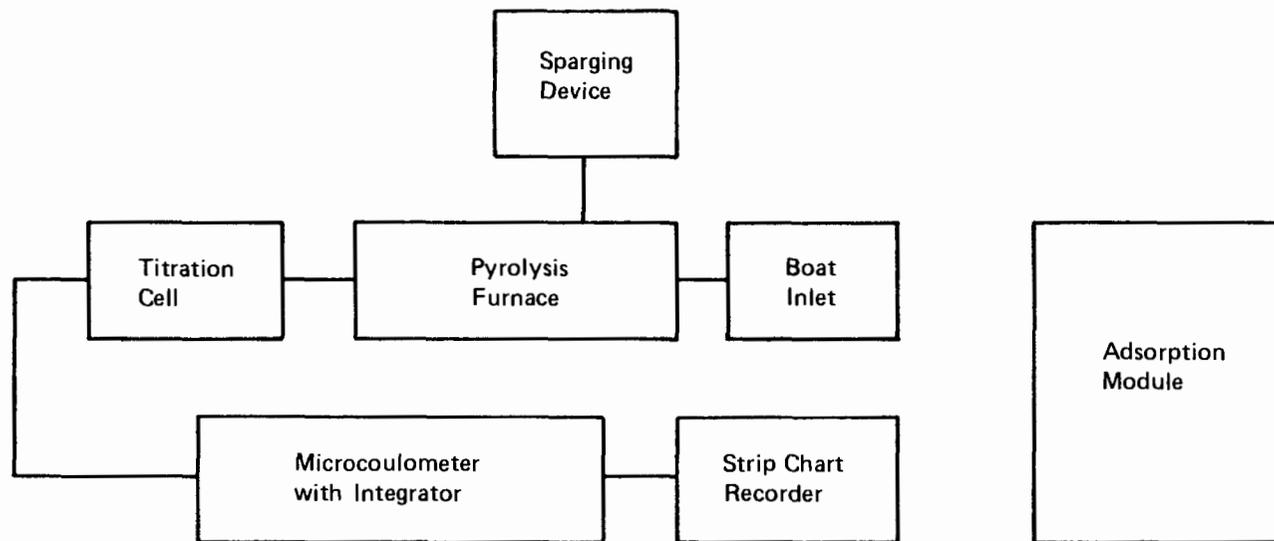


Figure 2. Schematic diagram of CAOx analysis system.

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5.12 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.13 Blank standard: The reagent water used to prepare the calibration standard should be used as the blank standard.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 All samples should be collected in bottles with teflon septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass, 250-ml, fitted with teflon-lined caps. Foil may be substituted for teflon if the sample is not corrosive. Samples must be protected against loss of volatiles by eliminating headspace in the container. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400° C before use, to minimize contamination.

6.3 All glassware must be dried prior to use according to the method discussed in 3.1.1.

### 7.0 Procedure

#### 7.1 Sample preparation

7.1.1 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

7.1.2 Reduce residual chlorine by adding sulfite (1 ml of 0.1 M per liter of sample). Sulfite should be added at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at 4° C without headspace.

7.1.3 Adjust the pH of the sample to approximately 2 with concentrated HNO<sub>3</sub> just prior to adding the sample to the reservoir.

#### 7.2 Calibration

7.2.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 ml of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2.2 Nitrate-wash blanks (method blanks): Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations. The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.2.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

### 7.3 Adsorption procedure

7.3.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

7.3.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 ml/min. NOTE: 100 ml of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/l; 50 ml for 501 to 1000 µg/l, and 25 ml for 1001 to 2000 µg/l.

7.3.3 Wash the columns-in-series with 2 ml of the 5000-mg/l nitrate solution at a rate of approximately 2 ml/min to displace inorganic chloride ions.

### 7.4 Pyrolysis procedure

7.4.1 The contents of each column are pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

7.4.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO<sub>2</sub>-rich atmosphere at a low temperature to ensure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O<sub>2</sub>-rich atmosphere. NOTE: The quartz sampling boat should have been previously muffled at 800° C for at least 2 to 4 min as in a previous analysis, and should be cleaned of any residue by vacuuming.

7.4.3 Transfer the contents of each column to the quartz boat for individual analysis.

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7.4.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCTS-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

7.4.5 Position the sample for 2 min in the 200° C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

7.4.6 After 2 min, advance the boat into the 800° C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 min to complete.

7.5 Detection: The effluent gases are directly analyzed in the micro-coulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

7.6 Breakthrough. The unpredictable nature of the background bias makes it especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10% of the two-column total measurement. If the 10% figure is exceeded, one of three events can be happening. Either (1) the first column was overloaded and a legitimate measure of breakthrough was obtained, in which case taking a smaller sample may be necessary; or (2) channeling or some other failure occurred, in which case the sample may need to be rerun; or (3) a high random bias occurred and the result should be rejected and the sample rerun. Because it may not be possible to determine which event occurred, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analysis that is rejected should be repeated whenever sample is available. If the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

7.7 Calculations: TOX as Cl<sup>-</sup> is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu\text{g/l Total Organic Halide}$$

where:

C<sub>1</sub> = μg Cl<sup>-</sup> on the first column in series

C<sub>2</sub> = μg Cl<sup>-</sup> on the second column in series

C<sub>3</sub> = predetermined, daily, average, method-blank value  
(nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in liters.

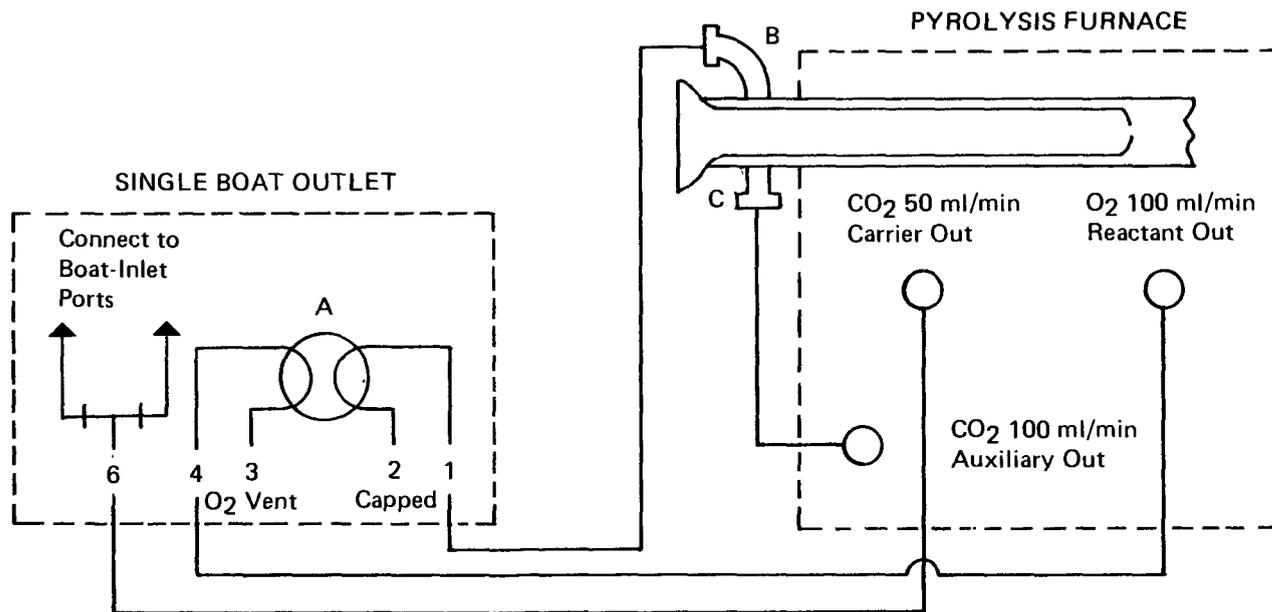


Figure 3. Rear-view plumbing schematic for MCTS-20 System. Valve A is set for first-stage combustion, O<sub>2</sub> venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

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### 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by analyzing appropriate quality-control check samples.

8.3 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

8.4 Employ a *minimum* of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Run check standard after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparations process.

8.7 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

## METHOD 9030

### SULFIDES

#### 1.0 Scope and Application

1.1 Method 9030 is used to measure the concentration of total and dissolved sulfides in drinking, surface and saline waters, and domestic and industrial wastes. The method does not measure acid-insoluble sulfides; copper sulfide is the only common acid-insoluble sulfide. Method 9030 is suitable for measuring sulfide in concentrations above 1 mg/l.

#### 2.0 Summary of Method

2.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back-titrated with sodium thiosulfate or phenylarsine oxide.

#### 3.0 Interferences

3.1 Reduced sulfur compounds that decompose in acid, such as sulfite, thiosulfate and hydrosulfite, may yield erratic results. Also, volatile iodine-consuming substances will give high results.

3.2 Samples must be taken with a minimum of aeration in order to avoid volatilization of sulfides and reaction with oxygen which may convert sulfide to unmeasurable forms.

3.3 If the sample is not preserved with zinc acetate, analysis must start immediately.

#### 4.0 Apparatus and Materials

4.1 Ordinary laboratory glassware.

#### 5.0 Reagents

5.1 Hydrochloric acid, HCl, 6 N.

5.2 Phenylarsine oxide 0.0250 N: Commercially available.

5.3 Starch indicator: Commercially available.

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5.4 Potassium iodide, KI crystals.

5.5 Amylose indicator.

5.6 Standard iodine solution, 0.0250 N: Dissolve 20 to 25 g KI in a little water in a liter volumetric flask and add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.0250 N sodium thiosulfate or phenylarsine oxide using a starch indicator, as follows.

5.6.1 Dissolve approximately 2 g (+1 g) KI crystals in 100 to 150 ml distilled water.

5.6.2 Add 20 ml of the iodine solution to be standardized and dilute to 300 ml.

5.6.3 Titrate with 0.0250 N phenylarsine oxide (PAO) until a pale straw color occurs.

5.6.4 Add a small amount of amylose indicator and wait until a homogeneous blue color develops.

5.6.5 Continue titration drop by drop until the color disappears.

5.6.6 Run in duplicate.

5.6.7 Calculate normality by the following equation:

$$N_{I_2} = \frac{\text{ml PAO} \times 0.0250}{20}$$

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Aqueous samples must be preserved with zinc acetate or the analysis must be started immediately.

## 7.0 Procedure

7.1 Unprecipitated sample

7.1.1 Place a known amount of standard iodine solution into a 500-ml flask. The amount should exceed the amount of sulfide expected.

7.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.

7.1.3 Add 2 ml of 6 N HCl.

7.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.

7.1.5 If the iodine color disappears, add more iodine until the color remains. Record the total number of ml of the standard iodine used in performing steps 7.1.1 and 7.1.5.

7.1.6 Titrate with reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution) using the starch indicator until the blue color disappears. Record the number of ml used.

## 7.2 Precipitated samples

7.2.1 Add the reagents to the sample in the original bottle. Perform steps 7.1.1, 7.1.3, 7.1.5, and 7.1.6.

## 7.3 Dewatered samples

7.3.1 Return the glass-fiber filter paper that contains the sample to the original bottle. Add 200 ml of distilled water. Perform steps 7.1.1, 7.1.3, 7.1.5, and 7.1.6.

7.3.2 The calculations (Section 7.4) should be based on the original sample put through the filter.

7.4 Calculations. One ml of 0.0250 N standard iodine solution reacts with 0.4 mg of sulfide present in the titration vessel. Thus, the following equation should be used to calculate sulfide concentration:

$$\text{mg/l sulfide} = 400(A-B)/\text{ml sample}$$

where:

A = ml of 0.0250 N standard iodine solution

B = ml of 0.0250 N standard reducing sodium thiosulfate or phenylarsine oxide solution.

## 8.0 Quality Control

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

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8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination has occurred.

8.5 Analyze check standards after approximately every 15 samples.

8.6 Run one duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.7 Spiked samples or standard reference materials shall be periodically employed to ensure that correct procedures are being followed and that all equipment is operating properly.

METHOD 9040  
pH MEASUREMENT

1.0 Scope and Application

1.1 Method 9040 is used to measure the pH of aqueous wastes and those multiphasic wastes where the aqueous phase comprises at least 20% of the total volume of the waste.

2.0 Summary

2.1 The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode. The measuring device is calibrated using a series of solutions of known pH.

3.0 Interferences

3.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.

3.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.

3.3 Coatings of oily material or particulate matter can impair electrode response. These coatings can usually be removed by gentle wiping or detergent washing, followed by distilled water rinsing. An additional treatment with hydrochloric acid (1:9) may be necessary to remove any remaining film.

3.4 Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation or by calibrating the electrode-instrument system at the temperature of the samples. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This error is sample-dependent and cannot be controlled. It should, therefore, be noted by reporting both the pH and temperature at the time of analysis.

4.0 Apparatus and Materials

4.1 pH Meter: Laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

4.2 Glass electrode.

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4.3 Reference electrode: A silver-silver chloride or other reference electrode of constant potential may be used. NOTE: Combination electrodes incorporating both measuring and referenced functions are convenient to use and are available with solid, gel-type filling materials that require minimal maintenance.

4.4 Magnetic stirrer and Teflon-coated stirring bar.

4.5 Thermometer or temperature sensor for automatic compensation.

### 5.0 Reagents

5.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary. Preparation of reference solutions from these salts requires some special precautions and handling<sup>1</sup> such as low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

5.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. These commercially available solutions have been validated by comparison to NBS standards and are recommended for routine use.

### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples should be analyzed as soon as possible.

### 7.0 Procedure

#### 7.1 Calibration

7.1.1 Because of the wide variety of pH meters and accessories, detailed operation procedures cannot be incorporated into this method. Each analyst must be acquainted with the operation of each system and familiar with all instrument functions. Special attention to care of the electrodes is recommended.

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<sup>1</sup>National Bureau of Standards Special Publication 260.

7.1.2 Each instrument/electrode system must be calibrated at a minimum of two points that bracket the expected pH of the samples and are approximately three pH units or more apart. Various instrument designs may involve use of a "balance" or "standardize" dial or slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions until readings are within 0.05 pH units of the buffer solution value.

7.2 Place the sample or buffer solution in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. If field measurements are being made, the electrodes may be immersed directly in the sample stream to an adequate depth and moved in a manner to ensure sufficient sample movement across the electrode-sensing element as indicated by drift-free (less than 0.1 pH) readings.

7.3 If the sample temperature differs by more than 2°C from the buffer solution, the measured pH values must be corrected. Instruments are equipped with automatic or manual compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

7.4 Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Note and record sample pH and temperature. Repeat measurement on successive volumes of sample until values differ by less than 0.1 pH units. Two or three volume changes are usually sufficient.

## 8.0 Quality Control

8.1 Duplicate samples and check standards should be analyzed routinely.

8.2 Electrodes must be thoroughly rinsed between samples.

PAINT FILTER LIQUIDS TEST

1.0 Scope and Application

1.1 This method is used to determine the presence and/or concentration of free liquids in a representative sample of waste, or to separate the liquid and solid portions of a sample.

1.2 The method is used to determine compliance with 40 CFR 261.21, 261.22, 264.314, and 265.314.

2.0 Summary of Method

2.1 A predetermined amount of material is placed in a paint filter and the free liquid portion of the material is that portion which passes through and drops from the filter.

3.0 Interferences

3.1 Filter media was observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

4.0 Apparatus and Materials

4.1 Conical paint filter - mesh number 60. Available at local paint stores such as Sherwin-Williams and Glidden for an approximate cost of \$0.07 each.

4.2 Glass Funnel [If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least one inch of the filter mesh to protrude should be used to support the filter. The funnel is to be fluted or have a large open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder, of the liquid that passes through the filter mesh.]

4.3 Metal Ring or Tripod

4.4 Ring Stand

4.5 Graduated Cylinder, 100 ml.

~~4.6 Glass Rod, 6"~~ Revised 1985

~~4.7 Watch Glass (for use if percent free liquid or free liquid portion is desired)~~

~~5.0 Reagents~~

~~5.1 None.~~

## 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected according to the directions in Section One of this manual.

6.2 A 100 ml or 100g representative sample is required for the test. [If it is not possible to obtain a sample of 100 ml or 100g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 ml or 100g, i.e., 200, 300, 400 ml or g. However, when larger samples are used, analysts shall divide the sample into 100 ml or 100g portions and test each portion separately. If any portion contains free liquids the entire sample is considered to have free liquids. If the percent of free liquid in the sample needs to be determined, it shall be the average of the sub-samples tested.]

## 7.0 Procedure

[In order to determine compliance with 40 CFR 264.314 or 265.314 only Steps 7.1 through 7.4 should be used.]

7.1 Assemble test apparatus as shown in Figure 1.

7.2 Place sample in the filter. A funnel may be used to provide support for the paint filter.

7.3 Allow sample to drain for 5 minutes into the graduated cylinder.

7.4 Note any free liquid generated after this five minute period. If any liquids collect in the graduated cylinder then the material is deemed to contain free liquids, for purposes of 40 CFR 264.314 or 265.314.

Continue with Steps 7.5 through 7.7 to determine the percent free liquid or to prepare the liquid phase for further testing, if appropriate.

7.5 Read and record volume of liquid phase in graduated cylinder. Stir sample with glass rod, let stand undisturbed for an additional 15 minutes.

7.6 Read and record volume of liquid phase.

7.7 Calculate % change between the two 15 minute readings. If the difference is less than 10%, the test is complete. If the change is greater than 10%, repeat steps 7.5 through 7.7 until the change between successive readings is less than 10%.

### Calculations:

$$\frac{\text{Current Reading (ml)} - \text{Preceding Reading (ml)}}{\text{Preceding Reading (ml)}} \times 100 = \% \text{ Change}$$

$$\frac{\text{Total Liquid Phase (ml)}}{\text{Sample Size (ml)}} \times 100 = \% \text{ Free Liquid}$$

## 8.0 Quality Control

8.1 Duplicate samples should be analyzed on a routine basis.

open mouth in order to support the paint filter yet not interfere with the movement, to the graduated cylinder, of the material that passes through the filter mesh.]

4.3 Ring Stand and Ring, or Tripod.

4.4 Beaker or Graduated Cylinder, 100 ml.

#### 5.0 Reagents

5.1 None.

#### 6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected according to the directions in Section One of this manual.

6.2 A 100 ml or 100g representative sample is required for the test. [If it is not possible to obtain a sample of 100 ml or 100g that is sufficiently representative of the waste, the analyst may use larger size samples in multiples of 100 ml or 100g, i.e., 200, 300, 400 ml or g. However, when larger samples are used, analysts shall divide the sample into 100 ml or 100g portions and test each portion separately. If any portion contains free liquids the entire sample is considered to have free liquids. If the percent of free liquid in the sample needs to be determined, it shall be the average of the sub-samples tested.]

#### 7.0 Procedure

7.1 Assemble test apparatus as shown in Figure 1.

7.2 Place sample in the filter. A funnel may be used to provide support for the paint filter.

7.3 Allow sample to drain for 5 minutes into the graduated cylinder.

## METHOD 9095

### PAINT FILTER LIQUIDS TEST

#### 1.0 Scope and Application

1.1 This method is used to determine the presence of free liquids in a representative sample of waste.

1.2 The method is used to determine compliance with 40 CFR 264.314 and 265.314.

#### 2.0 Summary of Method

2.1 A predetermined amount of material is placed in a paint filter. If any portion of the material passes through and drops from the filter within the 5 minute test period, the material is deemed to contain free liquids.

#### 3.0 Interferences

3.1 Filter media was observed to separate from the filter cone on exposure to alkaline materials. This development causes no problem if the sample is not disturbed.

#### 4.0 Apparatus and Materials

4.1 Conical paint filter - mesh number 60. Available at local paint stores such as Sherwin-Williams and Glidden for an approximate cost of \$0.07 each.

4.2 Glass Funnel [If the paint filter, with the waste, cannot sustain its weight on the ring stand, then a fluted glass funnel or glass funnel with a mouth large enough to allow at least one inch of the filter mesh to protrude should be used to support the filter. The funnel is to be fluted or have a large

7.4 If any portion of the test material collects in the graduated cylinder in the 5 minute period, then the material is deemed to contain free liquids for purposes of 40 CFR 264.314 and 265.314.

8.0 Quality Control

8.1 Duplicate samples should be analyzed on a routine basis.

9095/4

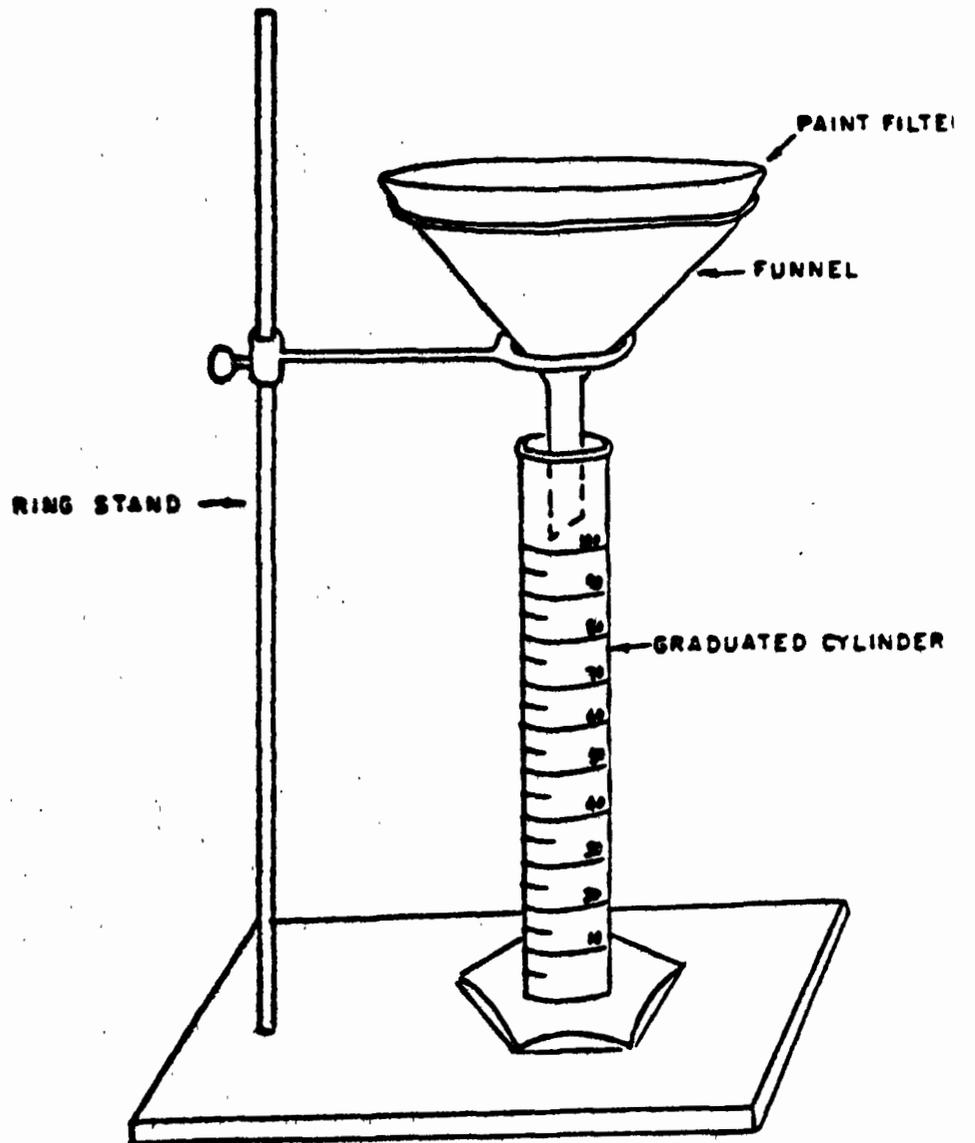


Figure 1. Free Liquid Apparatus.

## SECTION TEN

### QUALITY CONTROL/QUALITY ASSURANCE

Section 10.1 defines Quality Control (QC) and Quality Assurance (QA). Section 10.2 discusses how QC/QA procedures can be used to ensure achievement of program goals. The various QC/QA aspects of sampling are discussed in Section 10.1.3 while Section 10.1.4 discusses and lists appropriate laboratory QC/QA activities. Section 10.1.5 discusses the criteria with which acceptable data must comply and methods of data evaluation.

#### 10.1 Introduction

Quality assurance (QA) is a system for ensuring that all information, data, and resulting decisions compiled under a specific task are technically sound, statistically valid, and properly documented. Quality control is the mechanism through which quality assurance achieves its goals. Quality control programs define the frequency and methods of checks, audits, and reviews necessary to identify problems and dictate corrective action, thus verifying product quality.

The soundness of an organization's QC/QA program has a direct bearing on the integrity of its sampling and laboratory work. Results of sampling or analysis conducted without adequate quality control and assurance may be deemed unacceptable for RCRA evaluation purposes. The following section discusses some minimum standards for QC/QA programs. Generators who are choosing contractors to perform sampling or analytical work should make their choice only after evaluating the contractor's QC/QA program against the procedures presented in these sections. Likewise, contractors that currently sample and/or analyze solid wastes should similarly evaluate their QC/QA programs.

#### 10.2 Program Design

The initial step for any sampling or analytical work should be to strictly define the program goals. Once the goals have been defined, a program must be designed that will meet these program goals. QC and QA measures will be the mechanisms used to monitor the program and to ensure that all data generated are suitable for their intended use. A knowledgeable person who is not directly involved in the sampling or analysis must be assigned the responsibility of ensuring that the QC/QA measures are properly employed.

As a minimum, a proper QC/QA program would include the following:

1. The intended use(s) for the data, and the necessary level of precision and accuracy of the data for these intended uses.

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2. A representative sampling plan that includes provisions for:
  - selecting appropriate sampling locations, depths, etc.
  - providing a statistically sufficient number of sampling sites.
  - measuring all necessary ancillary data.
  - determining climatic flow or other conditions under which sampling should be conducted.
  - determining which media are to be sampled (e.g., wastewater, sediment, effluent, soil).
  - determining which parameters are to be measured (and where).
  - selecting appropriate sample containers.
  - selecting the frequency of sampling and length of sampling period.
  - selecting the types of sample (e.g., composites vs. grabs) to be collected.
  - sample preservation.
  - chain-of-custody.
3. An analytical plan that includes:
  - chain-of-custody procedures.
  - appropriate sample preparation methods.
  - appropriate analytical methods.
  - appropriate calibration and analytical procedures.
  - data handling, review and reporting.
4. Planning for the inclusion of proper and sufficient QC/QA activities, including the use of QC samples throughout all phases of the study to ensure that the level of quality of the data will meet the requirements of the intended use(s) of the data.

All program details should be put in writing and assignments made to appropriate personnel.

If the above procedures are followed (i.e., an appropriate program is designed, tasks are assigned to knowledgeable personnel, and sufficient QC/QA

steps are employed), the program should meet and possibly surpass its goals in most cases; at worst the failure to meet the program goals will be detected and the usefulness of any data will be quantified.

### 10.3 Sampling

The quality of a sampling program has a direct bearing on the legal, physical, and chemical integrity of the samples. If the representativeness of the samples cannot be verified due to inadequate attention to sampling procedures, then the usefulness of the analytical data will be limited, regardless of the refinement of the analytical program. It is imperative, therefore, that no analytical program be conducted without an adequate sampling plan which does or will document the degree of representativeness of the parameters of interest.

#### 10.3.1 Design of a Sampling Plan

Section One of this manual discusses the considerations involved in designing a representative sampling plan. For each specific project, a sampling plan should be designed prior to commencement of sampling. If the plan addresses the considerations discussed in Section One, then the resulting samples should be representative of the waste of interest and therefore suitable for evaluation of the waste according to RCRA criteria.

#### 10.3.2 Sample Collection

A variety of different sampling devices are used in sampling depending on the type of sample (solid, liquid, multiphased), the type of sample container, and the sampling location. Section One and portions of Section Three of this manual describe different devices that are available. The appropriate sampling device must be selected and its use supervised by a person thoroughly familiar with both the sampling and analytical requirements. This familiarity is essential since (1) certain sampling devices are made of materials that may contaminate samples, (2) cross contamination of samples can occur if the sampling device is not cleaned properly, (3) routine sampling methods may not be applicable when the waste is to be analyzed for a different parameter (e.g., volatile organic compounds), and (3) the method of employing the sampling devices may affect the integrity of the sample.

#### 10.3.3 Sample Preservation

Some form of preservation is usually required for all samples. The type of sample preservation required will vary depending on the sample type and the parameter to be measured. Therefore, more than one container of the same waste may be necessary if the waste is to be analyzed for more than one parameter type.

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The analytical methods included in this manual refer to the optimum means of preservation. Since the chemical make-up of certain samples can alter the effectiveness of preservation measures, all sample analyses should be performed as soon as possible after sampling and before any recommended holding time has expired.

##### 10.3.4 Chain of Custody

Although chain-of-custody procedures may not be required in all cases, they often are an essential part of sampling/analytical schemes since these procedures can document the history of samples. Chain of custody establishes the documentation and control necessary to identify and trace a sample from sample collection to final analysis. Such documentation includes labeling to prevent mix-up, container seals to detect unauthorized tampering with contents of the sample containers, secure custody, and the necessary records to support potential litigation.

A sample is considered to be under a person's custody if (1) it is in the person's physical possession, (2) in view of the person, (3) secured by that person so that no one can tamper with the sample, or (4) secured by that person in an area that is restricted to authorized personnel.

Refer to Section One for details of how to implement chain-of-custody procedures.

##### 10.4 Analysis

An analytical program defines standard operating procedures to be used in waste analysis, appropriate QC/QA procedures, means for detecting out-of-control situations, and remedial actions. A separate analytical program should be developed for each different waste to be analyzed. The program should be thoroughly specified before sampling is begun, since the analytical procedures to be used may affect the choice of sampling devices and procedures.

The program should select methods that will provide data at the level of accuracy and precision that will be required by users of the data for decision-making purposes under RCRA. Once the appropriate method(s) have been selected it is imperative that the accuracy and precision of all analytical data be thoroughly documented by means of a well-designed QC/QA program.

Laboratory QC/QA activities normally include:

1. Use of EPA-acceptable sample preparation and analytical methods.
2. Calibration of laboratory instruments to within acceptable limits according to EPA or manufacturer's specifications before, after, and during (as acceptable) use. Reference standards must be used when necessary.

3. Periodic inspection, maintenance, and servicing (as necessary) of all laboratory instruments and equipment.
4. The use of reference standards and QC samples (e.g., checks, spikes, laboratory blanks, duplicates, splits) as necessary to determine the accuracy and precision of procedures, instruments, and operators.
5. The use of adequate statistical procedures (e.g., QC charts) to monitor the precision and accuracy of the data and to establish acceptable limits.
6. A continuous review of results to identify and correct problems within the measurement system (e.g., instrumentation problems, inadequate operator training, inaccurate measurement methodologies).
7. Documenting the performance of systems and operators.
8. Regular participation in external laboratory evaluations (including the EPA Performance Audit Program) to determine the accuracy and overall performance of the laboratory. This should include performance evaluation and interlaboratory comparison studies, and formal field unit/laboratory evaluations and inspections.
9. Use of acceptable sample identification and, as necessary, formal chain-of-custody procedures in the laboratory.
10. Maintenance and storage of complete records, charts, and logs of all pertinent laboratory calibration, analytical, and QC activities and data.
11. Ensuring all data outputs are presented in their prescribed format.

Specific Quality Control measures for each method can be found by referring to the individual analytical methods included in this manual.

#### 10.5 Data Handling

The quality of all data must be assessed before the data are used. Assessment should focus on five basic points.

1. Accuracy - Can the data's accuracy be determined, and is it acceptable for the planned use? QC/QA procedures will be designed to measure the accuracy of all analytical data.
2. Precision - Can the data's precision be determined, and is it acceptable for the planned use? QC/QA should demonstrate the reproducibility of the measurement process.

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3. Completeness - Are a sufficient amount of data available for the planned use? QC/QA shall identify the quantity of data needed to meet the program goals.
4. Representativeness - How well do the data represent actual conditions at the sampling location, considering the original study design, sampling methods, analytical methods, etc., which were used?
5. Comparability - How comparable are data with respect to several factors, including:
  - consistency of reporting units?
  - standardized siting, sampling, and methods of analysis?
  - standardized data format?

All these factors must be considered when designing a study, and QC/QA procedures must specify a reviewing process for all data.

Statistical procedures applicable to data evaluation include:

1. Central tendency and dispersion
  - Arithmetic mean
  - Range
  - Standard deviation
  - Relative standard deviation
  - Pooled standard deviation
  - Geometric mean
2. Measures of variability
  - Accuracy
  - Bias
  - Precision; within laboratory and between laboratories
3. Significance test
  - u-test
  - t-test
  - F-test
  - Chi-square test

Specific data handling precautions are noted in the individual methods described in this manual.