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Solid Waste

EPA

Test Methods for Evaluating Solid Waste

Physical/Chemical Methods

SW846

TEST METHODS FOR EVALUATING SOLID WASTE

PHYSICAL/CHEMICAL METHODS

WASTE CHARACTERIZATION BRANCH

OFFICE OF SOLID WASTE

U.S. ENVIRONMENTAL PROTECTION AGENCY / MAY 1980

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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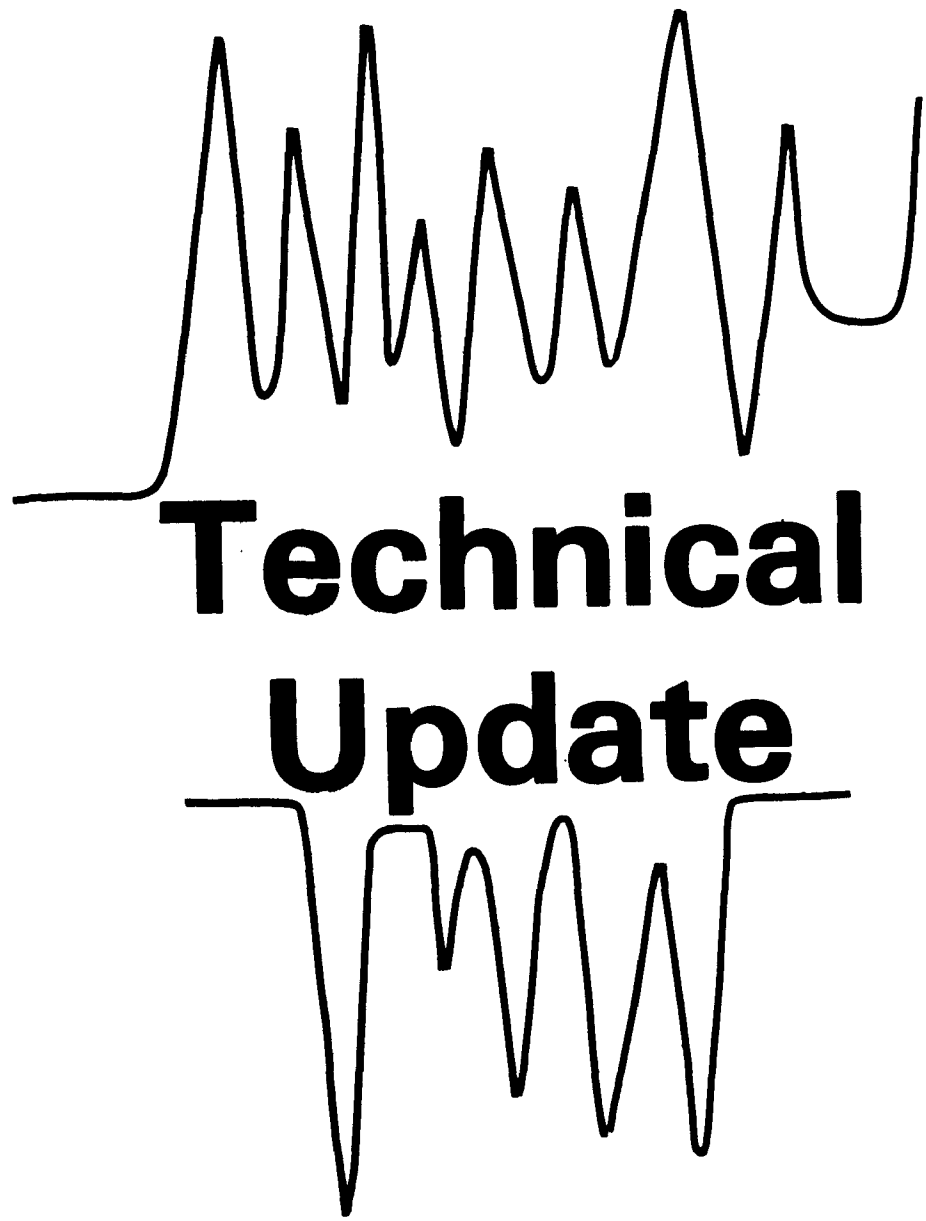

TEST METHODS FOR EVALUATING SOLID WASTE

PHYSICAL/CHEMICAL METHODS

Technical Update

This manual (SW-846B) updates the Test Methods for Evaluating Solid Waste (SW-846), and was written by the Hazardous and Industrial Waste Division of the Office of Solid Waste.

U.S. ENVIRONMENTAL PROTECTION AGENCY
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This publication (SW-846B) is the second revision to Test Methods for Evaluating Solid Waste (SW-846). Any mention of commercial products in the manual or this revision does not constitute endorsement by the U.S. Government. Editing and technical content were the responsibilities of the Hazardous and Industrial Waste Division, Office of Solid Waste.

Revision B 4/15/81

Table of Contents

8.09 Nitroaromatics

8.10 Polynuclear Aromatic Hydrocarbons

8.11 Haloethers [Reserved]

8.12 Semi-volatile chlorinated hydrocarbons, Not Otherwise Specified

8.13 Chlorinated Dibenzo-p-dioxins [Reserved]

8.22 Organophosphorus pesticides

8.40 Chlorophenoxy acid pesticides

Gas Chromatographic/Mass Spectroscopy Methods

8.24 Volatile organics

8.25 Semi-volatile organics

8.27 Capillary Column GC/MS Metod for the Analysis of Wastes

High Performance Liquid Chromatographic Methods

8.30 Polynuclear Aromatic Hydrocarbons [See method 8.10]

8.32 Carbamates [Reserved]

Atomic Absorption Spectrographic Methods

8.49 General Requirements

8.50 Antimony

8.51 Arsenic

8.52 Barium

8.53 Cadmium

8.54 Chromium

8.55 Cyanide

8.56 Lead

8.57 Mercury

8.58 Nickel

8.59 Selenium

8.60 Silver

INTRODUCTION

This first 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 promulated 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 Sections 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. The Agency anticipates that these methods will not be available before the later part of 1981.

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 acknowledgd and appreciated.

For the convenience of those using this manual, the above publications have been appended to this manual. Users are encouraged to review these additional sources of information prior to initiating laboratory work.

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, suggestion, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

1.0 Evaluation Plan Design

Purpose

40 CFR Part 262.11 requires generators to evaluate their waste in order to determine whether it meets the definition of a hazardous waste. On the basis of engineering evaluations of processes and their raw materials, many generators will elect to declare their waste hazardous without testing it. Other generators, who believe that their waste is not hazardous, will elect to test their waste in order to so demonstrate.

This section of the manual has two purposes. The first is to discuss relevant factors which generators should consider in developing a sampling and testing plan that provides maximum information at minimum cost. The second purpose is to outline for the regulated community standards of proof the Agency considers sufficient to demonstrate whether a waste does or does not possess a given property. Such demonstrations are necessary when generators petition the Agency under 40 CFR 260.20 and 260.22 to delist a waste. Such demonstrations are also crucial when the Agency determines that a waste meets the definition of a hazardous waste and the generator elects to challenge that determination. In such cases, conclusions regarding a waste's nature that are obtained using the procedures and standards of proof described in this manual will be accepted by the Agency as evidence that the determinations were made in good faith.

Why is there a need for such guidance?

The Agency has defined hazardous waste in terms of a waste's chemical and physical properties. If all wastes were perfectly homogeneous and if properties could be measured with 100% accuracy, there would be no need for this manual. In the real world, however, waste testing is far from simple or ideal. Errors can occur:

a. during the process of collecting a representative sample of the waste, unanticipated non-uniformity in the process generating the waste (i.e., due to changes in the waste's composition over time) or to the fact that the contaminants of concern in the waste are not uniformly distributed throughout the particular sample of waste (i.e., non-homogeneity), and

b. in analyzing the sample for the property of concern.

The discussion in this section of the manual pertains to how:

a. to design a sampling plan which yields a statistically representative sample of a waste,

b. to maximize the accuracy of an evaluation while minimizing the costs, and

c. to determine when a given waste has been adequately characterized.

Other sections of this manual will address the mechanics of collecting samples of a given batch or lot of waste, and of performing the laboratory procedures required to determine its physical or chemical properties.

The decision criteria presented in this section can be used by generators to determine if the evaluation of the waste is adequate to demonstrate that the true value for a specific property falls below the particular regulatory threshold value for that property.

Statistical Calculations

A statistic is a number that describes a certain aspect of a sample. The arithmetic mean (average) and standard deviation (s) are all statistics computed from a part of a populaton or universe (i.e., a sample).

The most useful statistics, and the ones to be used in determining the adequacy of the characterization, are the arithmetic mean of the sample ($\bar{x}$) and the standard deviation (s), which is a measure of the variability of the data obtained. These terms are defined as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Based on these statistical measures, a confidence interval can be developed within which the true value for the parameter being determined can be said to lie with a high degree of confidence. Thus if the upper bound of this interval (Upper Confidence Level (UCL)) is below the applicable threshold

then it can confidently be concluded to be non-hazardous. If, on the other hand, the UCL is above the threshold, then even though the values obtained for the samples tested fall below the threshold, one cannot confidently conclude the waste is not a a hazardous waste.

As will be discussed later, in developing a sampling plan and in collecting samples of a waste, it is important to insure that all portions of the waste have an equal chance of being represented. If representative samples are collected, the data obtained from testing will follow a normal distribution. In such cases, for purposes of waste characterization, the UCL can be calculated using the formula:

$$UCL = \bar{x} + \frac{(k')(s)}{\sqrt{n}} \quad \text{where}$$

k' is given in Table 1-1 and is a function of the number of samples tested.

Example:

A waste has a true concentration of cadmium of 10 mg/kg. The total waste was divided into 5 portions and each portion was analyzed to yield the following concentration values:

$X_1 = 5 mg/kg$

$X_2 = 15 mg/kg$

$X_3 = 15 mg/kg$

$X_4 = 8 mg/kg$

$X_5 = 7 mg/kg$

If the first and second portions had been selected as the random samples to test, the arithmetic mean would be identical to the population mean:

$$\bar{x} = (x_1 + x_2)/2 = (5 + 15)/2 = 10$$

If however, portions 4 and 5 had been selected, the arithmetic mean would be significantly different from the population mean:

$$\bar{x} = (X_4 + X_5/2 = (8 + 7)/2 = 7.5$$

Had portions 4 and 5 been selected, the UCL would still be reasonably close to the true value (e.g., within 10%).

$$x = 7.5$$

$$n = 2$$

$$s = \sqrt{[(8.0 - 7.5)^2 + (7.0 - 7.5)^2]/1}$$

$$= 0.7$$

$$UCL = 7.5 + k'(0.7)/\sqrt{2}$$

$$= 7.5 + (3.078)(0.7)/1.4$$

$$= 9.04$$

Table 1-1

n-1	k'
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	1.337
16	1.341
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
∞	1.282

n = Number of samples tested

Sampling Considerations

The physical characteristics of a waste determine the method of collecting samples as well as the number of samples that should be collected and tested before calculating an initial UCL. In evaluating wastes, it is impossible to have complete population data since only a very small fraction of the waste will be subjected to laboratory study. The objective of sampling, therefore, is to select a portion of the waste which is representative of the whole. In order to use the acceptance criteria described in this section, each component of the waste must have an equal chance of being sampled and tested. Therefore, before a sampling plan can be designed, the type of contamination distribution should be determined by an engineering analysis of the process generating the waste. The purpose of this analysis is to determine the appropriate sampling plan for obtaining a representative sample of the waste in question.

Wastes can be classified into six types depending on the uniformity of the process generating the waste and the homogeneity of the contaminant distribution within the waste. These categories determine the approach that should be used in conducting the sampling and the number of samples that should be tested initially. The six types of waste are:

I. Uniformly homogeneous

II. Non-uniformly homogeneous

III. Uniformly, randomly heterogeneous

IV. Non-uniformly, randomly heterogeneous

V. Uniformly, non-randomly heterogeneous

VI. Non-uniformly, non-randomly heterogeneous

In these classifications uniformity is defined as constancy of waste composition over a period of time. Homogeneity refers to the degree to which the components of the waste are uniformly distributed throughout the mass of waste (i.e., in a homogeneous sample all possible subsamples have an identical composition).

A Type I waste (uniformly homogeneous) is the one whose overall composition does not vary with time and for which the constituent of concern is evenly and randomly distributed throughout the waste (i.e., any single subsample of the whole would be expected to contain the same proportion of a given constituent as would any other subsample). Examples of wastes are liquid waste products disposed of on a regular basis (e.g., waste pesticide formulations remaining in holding tanks at the conclusion of a production run) and wastes generated from a well controlled manufacturing process (e.g., spent semiconductor etching solutions).

In Type II wastes, while any given unit quantity of the waste would be homogeneous, the nature of the process generating the waste is such that the overall composition changes with time. Such a situation might occur at a facility that uses batch processes to make a variety of similar products and which generates a well mixed, single phase liquid waste. While any portion of the waste generated from a given production

run would be equivalent, wastes from different runs would have different properties.

Types III through VI wastes are much more complex. Types III and V, deal with the cases where the composition of the waste as a whole remains the same, but the components are not uniformly distributed throughout the waste. In a randomly heterogeneous waste (Types III and IV) the likelihood is the same that any given sampling point will contain a specific type of contaminant. An example of a Type III waste is that generated by a batch plating operation that involves a number of plating processes, where all wastes feed into a single treatment facility, and where the sludge is stored in a tank that holds several weeks' worth of sludge. While the concentration of a given metal would not be uniform thoughout the tank, no one region within the tank is more likely to contain high concentrations of any one metal more than any other.

With Type V waste, placement of the waste is not random because of the nature of the storage or disposal process. For example, when a waste is discharged into a pond or lagoon, the heavier particles settle out first; thus, stratification occurs on a continuous basis. Samples of waste selected near the entrance point in the holding tank would always the more dense material. This is the reverse of the Type IV waste, in which no one type of waste is more likely than any

other to be found at a given point.

With Types I and III wastes, a simple random sample and a randomly prepared composite sample, respectively, will suffice as representative samples. With Type V wastes which may be stratified, the waste would have to be divided into a number of strata; each stratum would then have the properties of either a Type I or Type III waste. A random sample of each stratum would then be used to form a composite sample. The number of random subsamples collected from each stratum would then be a function of the relative proportion of that particular stratum in the waste as a whole. If, for example, dense particles comprised 50% of the waste and 10 subsamples were to be used in forming a composite, then 5 of those subsamples should be randomly collected from the dense particle substratum.

At this point, it should be mentioned that when the waste is non-uniform (i.e., Types II, IV, and VI), the generator would have to sample the waste over time. The techniques described herein for uniform wastes should be used in order to determine the significance of the changes with respect to the property of concern.

A major consideration in solid waste evaluation is the number of samples that should be tested. The sample size is determined by:

a. the degree of accuracy desired,

b. the cost of collecting and testing the samples, and

c. the variability of the population from which the samples are being taken (e.g., Type I wastes are exceedingly uniform and thus fewer samples would have to be tested whereas Type IV wastes are very variable and more samples would have to be tested).

As the number of samples tested increases, the confidence interval gets smaller (UCL approaches the mean) and the accuracy of the determination increases. At least 2 samples (the recommended minimum is 3 samples) must be collected and tested prior to calculating an initial average and upper confidence limit.

Testing Considerations

An additional aspect of waste testing that must be considered relates to the precision of the test methods used to measure the parameter of concern. The standard deviation of the values obtained when testing wastes is a function of both the sampling variability and the measurement variability, i.e.,:

$$S_o = f_1 S_s + f_2 S_a$$

where

S_o = overall standard deviation

S_s = standard deviation attributable to sampling error

S_a = standard deviation attributable to analytical error

f = complex function

In evaluating solid wastes, a number of testing procedures are used to determine if the waste is a hazardous waste. The precision of these methods varies not only as a function of the method used, but also as a function of the waste

matrix and the level of the property of interest (e.g., concentration of toxic species).

Where prior information is available that indicates the portion of the total testing error attributable to the measurement phase, the generator can use this information to determine the best (i.e., most cost effective) means of reducing the UCL. When S_a is high, then replicated measurements on the sample would tend to be more efficient than collecting and testing a larger number of samples. On the other hand, when S_a is low and S_s is high, larger numbers of samples should be evaluated. When S_a is unknown or cannot be estimated in advance, generators may find it cost effective to determine S_a during the initial experiments that are conducted to calculate UCL.

Once initial testing has been concluded and the UCL calculated, the decision on whether further testing is warranted depends upon several factors. Among these are:

a. relation of $\bar{x}$ and UCL to the threshold value,

b. cost of testing, and

c. relative cost of disposal as hazardous waste.

For example, if $\bar{x}$ is greater than the threshold value and (UCL $\bar{x}$) is small, there is a statistically small probability that the waste is not a hazardous waste, and thus there is little to be gained by further testing. If the UCL is less than the threshold value, the Agency will accept the conclusion drawn from such data and again there is little to be gained from futher testing. However, this acceptance by the Agency

is conditional on the generator's having used a sample collection plan that yields a sample that is representative of the whole, (as was discussed previously in this section). When the testing costs are low and the disposal costs are high, generators may want to do additional testing in order to increase the accuracy of the evaluation. One should keep in mind that the standard error is inversely proportional to the square root of the number of samples tested (e.g., increasing the number of samples tested from 4 to 16 reduces the standard error by 50%).

The Agency believes that, after taking these factors into account, each generator must make his own decisions as to the size of the testing program required to adequately evaluate a particular waste. The Agency will continue to expand material in this manual as new information develops in order to offer the regulated community further guidance and assistance.

Section 2.0

CHAIN OF CUSTODY CONSIDERATIONS

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 prevent unauthorized tampering with contents of the sample containers, secure custody, and the necessary records to support potential litigation.

Sample Labels

Sample labels (Figure 2.0-1) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate. The label must include at least the following information:

Name of collector.

Date and time of collection.

Place of collection.

Collector's sample number, which uniquely identifies the sample.

Collector _____ Collector's Sample No. _____

Place of Collection _____

Date Sampled _____ Time Sampled _____

Field Information _____

Figure 2.0-1

EXAMPLE OF SAMPLE LABEL

Sample Seals

Sample seals are used to preserve the integrity of the sample from the time it is collected until it is opened in the laboratory. Gummed paper seals may be used for this purpose. The paper seal must include, at least, the following information:

Collector's name.

Date and time of sampling.

Collector's sample number. (This number must be identical with the number on the sample label.)

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 2.0-2.

NAME AND ADDRESS OF ORGANIZATION COLLECTING SAMPLES

Person Collecting Sample _____ Collectors Sample No. _____
(Signature)

Date Collected _____ Time Collected _____

Place Collected _____

Figure 2.0-2

EXAMPLE OF OFFICIAL SAMPLE SEAL

Field Log Book

All information pertinent to a field survey and/or sampling must be recorded in a log book. This must be a bound book, preferably with consecutively numbered pages that are 21.6 by 27.9 cm (8 1/2 by 11 in.). Entries in the log book must include at least, 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, Fedeal Express)
- References such as maps or photographs of the sampling site.
- Field observations.
- Any field measurements made (e.g., pH, flammability, explositivity).

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.

Chain of Custody Record

To establish the documentation necessary to trace sample possession from the time of collection, a chain of custody record must be filled out and accompany every sample. This record becomes especially important when the sample is to be introduced as evidence in a court litigation. An example of a chain of custody record is illustrated in Figure 2.0-3.

The record must contain the following minimum information:

Collector's sample number.

Signature of collector.

Date and time of collection.

Place and address of collection.

Waste type.

Signatures of persons involved in the chain of possession.

Inclusive dates of possession.

Collector's Sample No. _____

CHAIN OF CUSTODY RECORD

Location of Sampling: ___ Producer ___ Hauler ___ Disposal Site

___ Other: _____

Sample

Shipper Name: _____

Address: _____

number street city state zip

Collector's Name _____ Telephone: (___)_____

signature

Date Sampled _____ Time Sampled _____hours _____

Type of Process Producing Waste _____

Field Information _____

_____

_____

Sample Receiver:

1. _____

name and address of organization receiving sample

2. _____

3. _____

Chain of Possession:

1. _____ _____ _____

signature title inclusive dates

2. _____ _____ _____

signature title inclusive dates

3. _____ _____ _____

signature title inclusive dates

Figure 2.0-3

EXAMPLE OF CHAIN OF CUSTODY RECORD

EXAMPLE OF CHAIN OF CUSTODY RECORD

Sample Analysis Request Sheet

The sample analysis request sheet (Figure 2.0-4) is intended to accompany the sample on delivery to the laboratory. The field portion of this form must be 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.

SAMPLE ANALYSIS REQUEST

PART I: FIELD SECTION

Collector _____ Date Sampled _____ Time _____ hours

Affiliation of Sampler _____

Address _____
number street city state zip

Telephone (___)_____ Company Contact _____

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 2.0-4

EXAMPLE OF HAZARDOUS WASTE SAMPLE ANALYSIS REQUEST SHEET

Sample delivery to the laboratory

Preferably, the sample must be delivered in person 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 2.0-3) and by a sample analysis request sheet (Figure 2.0-4). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

Shipping of Samples

A material 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 an appropriately sized glass or polyethylene container with non-metallic teflon lined screw cap. Allow sufficient ullage (approximately 10% by volume) so container is not liquid full at 54°C Celsius (130°). If sampling for volatile organic analysis, fill container to septum but use closed cap with space to provide an air space within the container. Large quantities, up to 3.785 liters (1 gallon), may be collected if the sample's flash point is $\geq$ 23°C (73°F). In this case, the flash point must be marked on the outside container (e.g., carton, cooler).

2. Seal sample and place in a 4 ml thick polyethylene bag, one sample per bag.

Liquids

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

   Address

   "Flammable Liquid N.O.S."

   (or "Flammable Solid N.O.S.")

Note: Using "Flammable" does not convey the certain knowledge that a sample is flammable but is intended to prescribe the class of packing needed to comply with DOT regulations.

5. Place one or more metal cans in a strong outside container such as a picnic cooler or fiberboard box. Ice or dry ice may be used between the metal cans and the outside container and must be contained to avoid water leakage during transport. No other preservatives are allowed.

6. Complete carrier's certification form as shown in Figure 2.0-5.

7. Samples may be transported by rented or common carrier truck, bus, railroad, and entities such as Federal Express* but not by normal common carrier air transport even on a "cargo only" aircraft.

*These procedures are designed to enable shipment by entities like Federal Express; however, they should not be construed as an endorsement by EPA of a particular commercial carrier.

Solids

3. Place sealed bag inside cushioned overpack. If sample is expected to undergo change during shipment cool using dry or wet ice. Overpack must be designed to prevent water leakage during transport. No other preservatives are allowed.
4. Complete carrier's certification form as shown in Figure 2.0-5.
5. Samples may be transported by rented or common carrier truck, bus, railroad, and entities such as Federal Express* but not by normal common carrier air transport even on a "cargo only" aircraft.

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 walls show

*These procedures are designed to enable shipment by entities like Federal Express; however, they should not be construed as an endorsement by EPA of a particular commercial carrier.

the sample is under pressure or releasing gases, respectively, it should be treated with caution. The sample can be explosive or release extremely poisonous gses. 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. Discrepancies between the information on the sample label and seal and that 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.

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 supervisor should then decide what analyses are to be performed. The sample may have to be split with other laboratories to obtain the necessary information about the sample. The supervisor should decide on the sample location and delineate the types of analyses to be performed on each allocation. In his own laboratory, the supervisor should assign the sample analysis to at least one analyst, who is to be responsible for the care and custody of the sample once it is received. 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.

The receiving analyst 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.

Section 3.0

SAMPLING METHODOLOGY

Introduction

This section describes the equipment and procedures which the Agency has determined are suitable for use in obtaining a representative sample of a solid waste.

Because the types of solid waste regulated under RCRA cover a very broad range of physical and chemical types, the information in this section will of necessity be general in nature. It is incumbent upon those persons conducting sampling programs to exercise caution when using the methods described herein.

Sub-Section 3.2

SAMPLING EQUIPMENT

Introduction

Sampling the diverse types of RCRA regulated wastes requires a variety of different types of samplers. A number of such sampling devices are described in this section. While some of these samplers are commercially available, others will have to be fabricated by the user. Table 3.2-1 is a general guide to the types of waste that can be sampled by each of the samplers described.

Table 3.2-1

SAMPLING EQUIPMENT FOR PARTICULAR WASTE TYPES

Sampling Point / Waste Type	Drum	Sacks and Bags	Open Bed Truck	Closed Bed Truck	Storage Tanks or Bins	Waste Piles	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	N/A		N/A	N/A
Moist Powders or Granules	Trier	Trier	Trier	Trier	Trier	Trier	Trier	Shovel	
Dry Powders or Granules	Thief	Thief	Thief	Thief	Thief	Thief	Thief	Shovel	
Sand or Packed Powders and Granules	Auger	Auger	Auger	Auger				N/A	
Large Grained Solids	arge Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	Large Trier	

3.2.1 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 in sampling wastes which consist of a number of 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 and their report, "Samplers and Sampling Procedures for Hazardous Waste Streams" [Appendix I of this manual] should be consulted.

General Comments and Precautions

1. Do not use a plastic Coliswasa to sample wastes containing organic materials.
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

Coliwasas are not available commercially and must be fabricated to conform to the specifications detailed in Figure 3.2-1. Table 3.2-2 lists the parts required to fabricate a plastic or glass Coliwasa.

Table 3.2-2

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 channnel	Fabricate from aluminum bar stock	Hardware stores

Quantity	Item	Comments	Supplier
1	Swivel, aluminum bar 1.27 cm square x 5.08 cm long with 3/8" NC inside thread to attach stopper rod	Fabricate from aluminum bar stock	hardware stores
1	Nut, PVC, 3/8" NC		Plastic supplier
1	Washer, PVC, 3/8" NC		Plastic supplier
1	Nut, stainless steel, 3/8" NC		Hardware stores
1	Washer, stainless steel, 3/8"		Hardware stores
1	Bolt, 3.12 cm long x 3/16" NC		Hardware stores
1	Nut, 3/16" NC		Hardware stores
1	Washer, lock 3/16"		Hardware stores

Assembly

Assemble sampler as follows:

1. Attach swivel to the T-handle with the 3.12cm long bolt and secure with the 3/16" 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" 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 hole 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 insure it is leak free.

Procedure

1. Clean Coliwasa.
2. Adjust sampler's locking mechanism to insure 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 which 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 non-representative 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.
6. Place sample tube at mouth of a container and discharge sample by slowly opening the sampler.

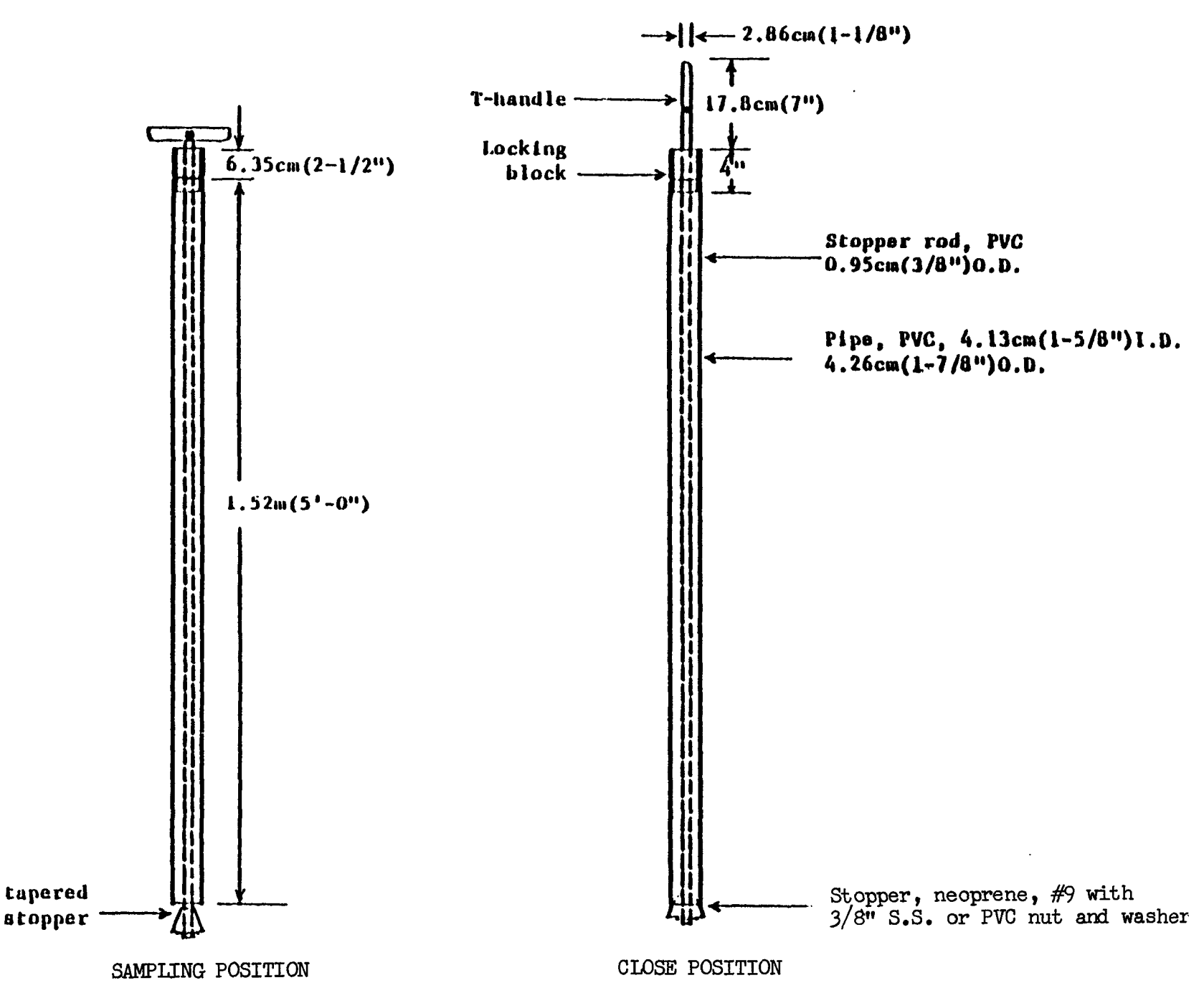


Figure 3.2-1
COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

3.2.2 Weighted Bottle

Scope and Application

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

General Comments and Precautions

1. Do not use a 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 insure 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 3.2).

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.

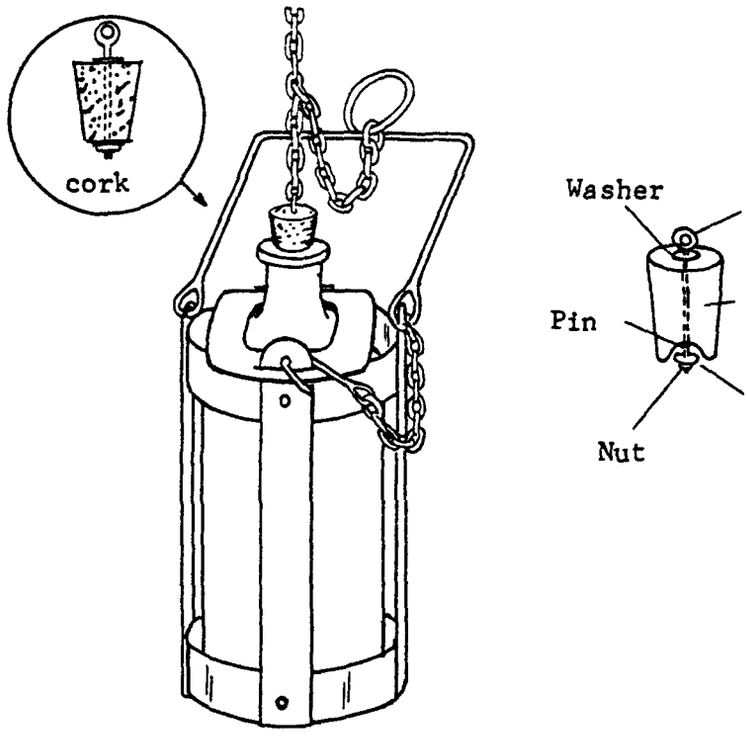


Figure 3.2
WEIGHTED BOTTLE SAMPLER

3.2.3 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 plastic beaker to sample wastes containing organic materials.
2. Do not use a glass beaker to sample wastes of high pH or which 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 confrom to the specifications detailed in Figure 3.2-3. Table 3.2-3 lists the parts required to fabricate a dipper.

Table 3.2-3
PARTS FOR CONSTRUCTING A DIPPER

Quantity	Item	Supplier
1	Adjustable clamp, 6.4 to 8.9 cm (2 1/2 to 3 1/2") for 250 to 600 ml beakers. Heavy duty aluminum.	Laboratory supply houses
1	Tube 2.5 to 4.5 meters long with joint cam locking mechanism. Diameter 2.54 cm ID and 3.18 cm ID.	Swimming pool supply houses

Quantity	Item	Supplier
1	Polypropylene or glass beaker, 250 ml to 600 ml.	Laboratory supply houses
4	Bolts 2 1/4" x 1/4", NC	Hardware stores
4	Nuts, 1/4", NC	Hardware stores

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.

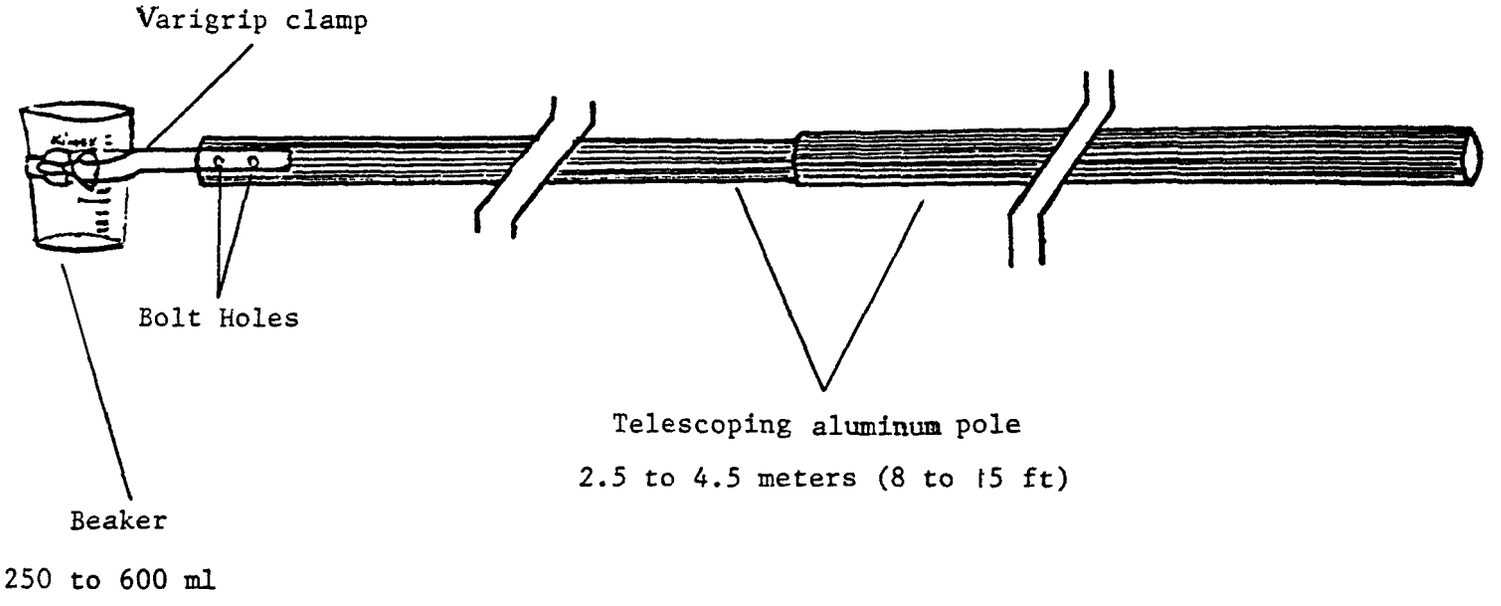


Figure 3.2-3
DIPPER

3.2.4 Thief

Scope and Appication

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 1/3 the width of the slots.

Apparatus

A thief is available at laboratory supply stores. (Figure 3.2-4)

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.

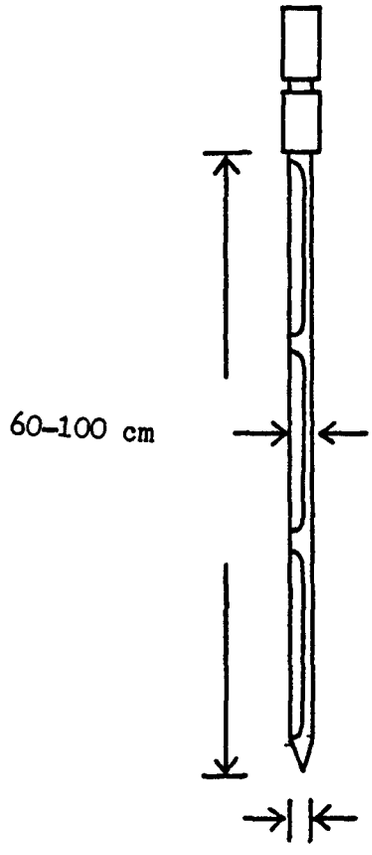


Figure 3.2-4
THIEF SAMPLER

3.2.5 Trier

Scope and Application

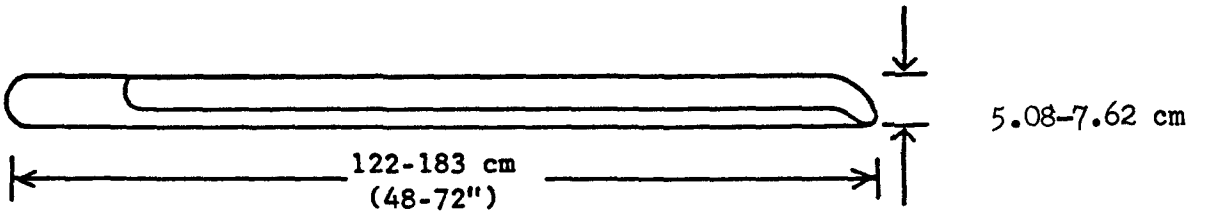
A trier consists of a tube cut in half lengthwise with a sharpened tip that allows the sampler to cut into sticky solids and loosen soil. A trier samples moist or sticky solids with a particle diameter less than 1/2 the diameter of the trier.

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 confrom to the specifications in Figure 3-5. A metal or polyvinyl chloride pipe 1.52 m (5') long x 3.2 cm (1.4") I.D. with a 0.32 cm (1 1/8") 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.

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.



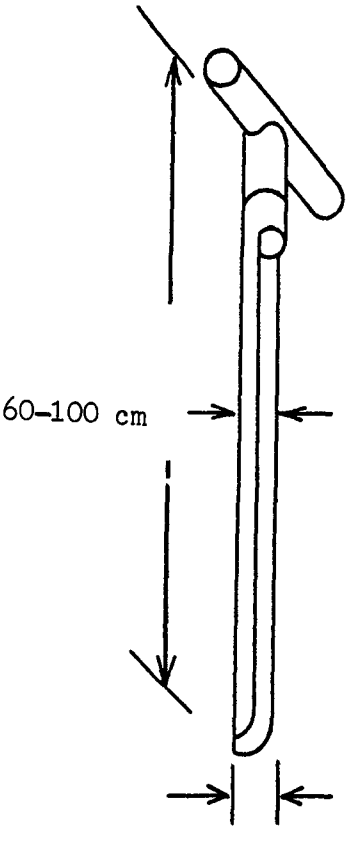


Figure 3.2-5
SAMPLING TRIERS

3.2.6 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.

Procedures

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.

3.2.7 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 with the scoop or shovel large enough to contain the waste collected in one cross section sweep.

Sub-Section 3.3

SAMPLE CONTAINERS

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 required volume of sample or the entire volume of a sample contained in samplers.

Plastic and glass containers are generally used for collecting and storing of hazardous waste samples. Commonly available plastic containers are made of high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, teflon FEP (flourinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is almost universally usuable due to its chemical inertness and resistance to breakage. However, its high cost severely limits its use. LPE, on the other hand, offers the best combination of chemical resistance and low cost when inorganic wastes are involved.

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 hydroflouric acid. Soda glass bottles are suggested due to their low cost and ready availability. Borosilicate glass containers, such as Pyrex and Corex, have advantages relative to inertness and resistance to breakage respectively 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. These caps are usually provided with waxed paper liners. Other liners that may be suitable are polyethylene, polypropylene, neoprene, and teflon FEP plastics. Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Maryland 21133).

Section 4

IGNITABILITY

Introduction

The objective of the ignitability characteristic is to identify wastes which present fire hazards due to being ignitable under routine storage, disposal, and transportation and wastes capable of severely exacerbating a fire once started.

Sub-Section 4.1

CHARACTERISTIC 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 percent 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 a Setaflash Closed Cup Tester, using the test method specified in ASTM standard D-3278-78, 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 of 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.

* ASTM Standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.

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.

Sub-Section 4.4

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 p.s.i. at 70°F or, regardless of the pressure at 70°F, having an absolute pressure exceeding 104 p.s.i. at 130°F, or any liquid flammable material having a vapor pressure exceeding 40 p.s.i. absolute at 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 percent or less (by volume) with air forms a flammable mixture or the flammable range with air is wider than 12 percent 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.

Sub-Section 4.5

OXIDIZER

An oxidizer for the purpose of this regulation is any material that yields oxygen readily to stimulate the combustion of organic matter (e.g., chlorate, permanganate, peroxide, nitro carbo nitrate, inorganic nitrate).

Section 5

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:

a. Mobilize toxic metals if discharged into a landfill environment.

b. Require handling, storage, tranportation and management equipment to be fabricated of specially selected materials of construction, and

c. Destroy human or animal tissue in the event of inadvertant contact.

In order to identify such potentially hazardous materials, the Agency has selected several properties upon which to base the definition of a corrosive waste. These properties are pH and corrosivity toward Type SAE 1020 steel. The following section presents methodology for measuring the pH of aqueous wastes and for determining whether the waste is corrosive to steel.

Sub-Section 5.1

CHARACTERISTIC OF CORROSIVITY REGULATION

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 the "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods"* (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 "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods," or an 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.

*This document is available from Solid Waste Information, U.S. Environmental Protection Agency, 26 W. St. Clair Street, Cincinnati, Ohio 45268

**The NACE Standard is available from the National Association of Corrosion Engineers, P.O. Box 986, Katy, Texas 77450

Method 5.2

pH MEASUREMENT

Scope and Application

This method* is applicable to aqueous wastes and those multiphasic wastes where the aqueous phase comprises at least 20% of the total volume of the waste.

Summary

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.

Interferences

1. The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
2. Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
3. Coatings of oily material or particulate matter can impair electrode response. These coating 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.

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*This method has been adapted from Method 150.1 of "Methods for the Analysis of Water and Wastewater", EPA-6000/4-79-020, U.S. EPA, EMSL, Cincinnati, OH 45268

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 is the change of pH inherent in the sample at various temperatures. 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.

Apparatus

1. pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.
2. Glass electrode.
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. Magnetic stirrer and Teflon-coated stirring bar.
5. Thermometer or temperature sensor for automatic compensation.

Reagents

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[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

2. Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

Calibration

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.

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 and/or slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until

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[1] National Bureau of Standards Special Publication 260.

readings are within 0.05 pH units of the buffer solution value.

Procedure

1. Standardize the meter and electrode system as outlined in Section 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 insure sufficient sample movement across the electrode sensing element as indicated by drift free (<0.1 pH) readings.
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.
4. After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. 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 sufficent.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p. 460, (1975).

2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-65, p. 178, (1976).

Method 5.3

CORROSIVITY TOWARD STEEL

Introduction

This method† is applicable to either aqueous or non aqueous liquid wastes.

Summary of the Method

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.

Precautions and Comments

1. In laboratory tests, such as this one, corrosion of duplicate coupons is usually reproducible to within ± 10%. Occasional exceptions, in which large differences are observed, can occur under conditions where the metal surfaces become passivated. Therefore, at least duplicate determinations of corrosion rate should be made.
2. A circular specimen of about 3.75 cm (1.5 inch) diameter is a convenient shape for laboratory use. With a thickness of approximately 0.32 cm (0.125 inch) and a 0.80 cm (0.4 inch) diameter hold 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:

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†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

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

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.

3. 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. More uniform results may be expected if a substantial layer of metal is removed from the coupons prior to testing the corrosivity of the wste. This can be accomplished either by chemical treatment (pickling), electrolytic removal, or by grinding with a coarse abrasive. At least 0.000254 cm (0.0001 inch) or 2 to 3 mg/cm^2 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.
5. The minimum ratio of volume of waste to area of the metal coupon to be used in this test is 40 ml/cm^2.

Equipment

1. A versatile and convenient apparatus should be used, consisting of a kettle or flask of suitable size (usually 500 to 5000 millilieters), a reflex condenser with atmospheric

seal, 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.

2. The supporting device and container should not be affected by or cause contamination of the waste under test.
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.
4. The shape and form of the coupon support should assure free contact with the waste.

Test Procedure

1. Assemble the test apparatus as described the "Equipment" section above.
2. Fill the container with the appropriate amount of waste. (See #5 under the "Precautions and Comments" section.)
3. Begin agitation at a rate sufficient to insure that the liquid is kept well mixed and homogeneous.
4. Using the heating device bring the temperature of the waste to 55° C (130° F).
5. If the anticipated corrosion rate is moderate (i.e., <635 mmpy), the test should be run for at leat 200 hours to insure adequate weight loss to permit accurate results to be obtained. If the corrosion rate is low (i.e., >100 mmpy),

then the test duration should be on the order of 2000 hours. in cases where the anticipated corrosion rate is completely unknown, initial testing should be performed using a 200 hour duration.

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.

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.

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:

Solution	Soaking Time	Temperature
20% NaOH + 200g/l zinc dust	5 min	Boiling
or		
Conc. HCl + 50g/l $SnCl_2$ + 20g/l $SB^{-1}3$	Until clean	Cold

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

Solution	50 g/l H_2SO_4
Anode	Carbon or lead
Cathode	Steel coupon
Cathode current density	20 amp/cm^2 (129 amp/in^2)
Inhibitor	2 cc organic inhibitor/liter
Temperature	74°C (165°F)
Exposure Period	3 minutes

Note: Precautions must be taken to insure good electrical contact with the coupon, to avoid contamination of the cleaning solution with easily reducible metal ions, and to insure 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.

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. 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 required 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 purpose of this requlation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{\text{(weight loss) (0.268)}}{\text{(area) (time)}}$$

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

5.3-7

technical practices committees

NATIONAL ASSOCIATION OF CORROSION ENGINEERS

NACE Standard TM-01-69
(1972 Revision)

Test Method

Laboratory Corrosion Testing of Metals for the Process Industries

Approved March, 1969
Revised August, 1972
National Association of Corrosion Engineers
2400 West Loop South
Houston, Texas 77027
713/622-8980

The National Association of Corrosion Engineers issues this Standard in conformity to the best current technology regarding the specific subject. This Standard represents minimum requirements and should in no way be interpreted as a restriction on the use of better procedures or materials. Neither is this Standard intended to apply in any and all cases relating to the subject. Numerous external factors may negate the usefulness of this Standard in specific instances.

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Foreword

Unit Committee T-5A ("Corrosion in Chemical Processes") of the National Association of Corrosion Engineers issues this Standard with a dual purpose.

The first purpose is to standardize, as much as possible, simple immersion corrosion studies. In this sense, this Standard is reasonable and effective without imposing inflexible requirements as to apparatus, conditions, or techniques. The actual conditions of test will be determined by the problem at hand and limited only by the ingenuity of the individual investigator.

The second purpose of this Standard is to present to the user a consensus on the best current technology in this field of laboratory corrosion testing. As such, this Standard enumerates and discusses the many factors which must be considered, controlled, and reported in order to aid in correlation or reproducibility of such studies.

The techniques described permit the investigator to reproduce to a considerable extent in the laboratory, through judicious experimental design, the process conditions which govern corrosion mechanisms. The tests are not to be construed as "accelerated" tests, which are generally unreliable. The methods described are also applicable to materials qualification tests for quality control. However, the latter require more rigid definition of apparatus, conditions, and technique.

The ultimate purpose is better correlation of results in the future and the reduction of conflicting reports through a more detailed recording of meaningful factors and conditions.

TEST METHOD

Laboratory Corrosion Testing of Metals for the Process Industries

CONTENTS

Additional copies of this NACE Standard are available at $2 per copy from NACE Headquarters, 2400 West Loop South, Houston, Texas 77027.

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1. General

1.1 This Standard describes the factors which influence laboratory tests. These factors include specimen preparation, apparatus, test conditions (solution composition, temperature, velocity, aeration, volume, method of supporting specimens, duration of test), methods of cleaning specimens, evaluation of results, and calculation of corrosion rates. This Standard also emphasizes the importance of recording all pertinent data and provides a check list for reporting test data.

1.2 Experience has shown that all metals and alloys do not respond alike to the many factors that control corrosion and that "accelerated" corrosion tests give indicative results only. Consequently, it is impractical to propose an inflexible standard laboratory corrosion testing procedure for general use except for material qualification tests, where standardization is obviously required.

1.3 In designing any corrosion test, consideration must be given to the various factors discussed in this test method because these factors have been found to affect greatly the results obtained.

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2. Specimen Preparation

2.1 In laboratory tests, corrosion rates of duplicate specimens are usually within ± 10% under the same test conditions. Occasional exceptions, in which a large difference is observed, can occur under conditions of borderline passivity of metals or alloys that depend on a passive film for their resistance to corrosion. Therefore, at least duplicate specimens should be exposed in each test.

2.2 If the effects of corrosion are to be determined by changes in mechanical properties, untested duplicate specimens should be preserved in a non-corrosive environment for comparison with the corroded specimens. The mechanical property commonly used for comparison is the tensile strength. The procedure for determining this value is shown in detail in ASTM Standard E-8- latest edition.

2.3 The size and the shape of specimens will vary with the purpose of the test, nature of the materials, and apparatus used. A large surface-to-mass ratio and a small ratio of edge area to total area are desirable. These ratios can be achieved through the use of rectangular or circular specimens of minimum thickness. Circular specimens should be cut preferably from sheet and not bar stock to minimize the exposed end grain.

2.3.1 A circular specimen of about 1 1/2-inch diameter is a convenient shape for laboratory corrosion tests. With a thickness of approximately 1/8 inch and a 5/16 or 7/16-inch 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:

$$A = \frac{\pi}{2}(D^2 - d^2) + t\pi D + t\pi d$$

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 ($t\pi d$) in the equation is omitted.

2.3.2 Strip coupons (of about 4 square inches) may be preferred as corrosion specimens, particularly if interface or liquid line effects are to be studied by the laboratory test, but such effects are beyond the scope of this Standard.

2.3.3 All specimens should be measured carefully to permit accurate calculation of the exposed areas. An area calculation accurate to plus or minus 1% is usually adequate.

2.4 More uniform results may be expected if a substantial layer of metal is removed from the specimens to eliminate variations in condition of the original metallic surface. This can be done either by chemical treatment (pickling), electrolytic removal, or by grinding with a coarse abrasive paper or cloth, such as No. 50, using care not to work harden the surface (see Section 2.7). At least 0.0001 inch or 10 to 15 milligrams per square inch should be removed. If clad alloy specimens are to be used, special attention must be given to insure that excessive metal is not removed. After final preparation of the specimen surface, the specimens should be stored in a desiccator until exposure if they are not used immediately.

2.5 Exposure of sheared edges should be avoided unless the purpose of the test is to study effects of the shearing operation. It may be desirable to test a surface representative of the material and metallurgical condition used in practice.

2.6 The specimen can be stamped with an appropriate identifying mark.

2.6.1 The stamp, besides identifying the specimen, introduces stresses and cold work in the specimen, that could be responsible for localized corrosion and/or stress corrosion cracking.

2.6.2 Stress corrosion cracking at the identifying mark is a positive indication of susceptibility to such

corrosion; however, the absence of cracking should not be interpreted as indicating resistance. Additional tests should be run to study specifically the effects of stress.

2.7 Final surface treatment of the specimens should include finishing with No. 120 abrasive paper or cloth, or the equivalent, unless the surface is to be used in the mill-finished condition. This resurfacing may cause some surface work-hardening to an extent which will be determined by the vigor of the surfacing operation but is not ordinarily significant.

2.7.1 Coupons of different alloy compositions should never be ground on the same cloth.

2.7.2 Wet grinding should be used on alloys which work harden quickly, such as the austenitic stainless steels.

2.8 The specimens should be finally degreased by scrubbing with bleach-free scouring powder, followed by thorough rinsing in water and in a suitable solvent (such as acetone, methanol, or a mixture of 50% methanol and 50% ether) and air dried. For relatively soft metals such as aluminum, magnesium, and copper, scrubbing with abrasive is not always needed and can mar the surface of the specimen. The use of towels for drying may introduce an error through contamination of the specimens with grease or lint.

2.9 The dried specimens should be weighed on an analytical balance to an accuracy of plus or minus 0.5 milligram.

2.10 The method of specimen preparation should be described when reporting tests results to facilitate interpretation of data by other persons.

2.10.1 Reports should include trade name or composition of specimens in the following order of preference: (a) chemical composition determined by analysis, (b) approximate or nominal chemical composition, and (c) trade name or grade and specification (if bought to MIL, ASTM, etc.)

2.10.2 Metallurgical condition of the specimens, including the degree of hot or cold working and heat treatment, should be described as completely as possible.

2.11 The use of welded specimens is often desirable because some welds may be cathodic or anodic to the base metal and may affect the corrosion.

2.11.1 The heat-affected zone is also of importance but should be studied separately because welds on coupons do not faithfully reproduce heat input or size effects of full-size vessels.

2.11.2 Corrosion of a welded coupon is best reported by description and thickness measurements rather than a mils-per-year rate because the attack is normally localized and not representative of the entire surface.

2.11.3 A complete discussion of corrosion testing of welded coupons or the effect of heat treatment on the corrosion resistance of a metal is not within the scope of this Standard.

3. Equipment and Apparatus

3.1 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 with atmospheric seal, a sparger for controlling atmosphere or aeration, a thermowell and temperature regulating device, a heating device (mantle, hot plate, or bath), and a specimen support system. If agitation is required, the apparatus can be modified to accept a suitable stirring mechanism such as a magnetic stirrer. A typical resin flask set up for this type test is shown in Figure 1.

3.2 These suggested components can be modified, simplified or made more sophisticated to fit the needs of a particular investigation. The suggested apparatus is basic, and the apparatus is limited only by the judgment and ingenuity of the investigator.

3.2.1 A glass reaction kettle can be used where configuration and size of specimens will permit entry through the narrow kettle neck.

3.2.2 In some cases, a wide mouth jar with a suitable closure is sufficient when simple immersion tests at ambient temperatures are to be investigated.

3.2.3 Open beaker tests should not be used because of evaporation and contamination.

3.2.4 In more complex tests, provisions might be needed for continuous flow or replenishment of the corrosive liquid while simultaneously maintaining a controlled atmosphere.

4. Test Conditions

4.1 Selection of the conditions for a laboratory corrosion test will be determined by the purpose of the test.

4.1.1 If the test is to be a guide for the selection of a material for a particular purpose, the limits of controlling factors in service must be determined. These factors include oxygen concentration, temperature, rate of flow, pH value, and other important characteristics of the solution.

4.2 An effort should be made to duplicate all service conditions in the corrosion test.

4.3 It is important that test conditions be controlled throughout the test in order to ensure reproducible results.

4.4 The spread in corrosion rate values for duplicate specimens in a given test probably should not exceed ± 10% of the average when the attack is uniform.

4.5 Composition of solution.

4.5.1 Test solutions should be prepared accurately from chemicals conforming to the Standards of the Committee on Analytical Reagents of the American Chemical Society,[1] and distilled water, except in those cases where naturally occurring solutions or those taken directly from some plant process are used.

4.5.2 The composition of the test solution should be controlled to the fullest extent possible and should be described as completely and as accurately as possible when the results are reported.

4.5.2.1 Minor constituents should not be overlooked because they often affect corrosion rates.

4.5.2.2 Chemical content should be reported as percentage by weight of the solution. Molarity and normality are also helpful in defining the concentration of chemicals in the test solution.

4.5.3 The composition of the test solution should be checked by analysis at the end of the test to determine the extent of change in composition, such as might result from evaporation.

4.5.4 Evaporation losses should be controlled by a constant level device or by frequent additions of appropriate solution to maintain the original volume within ± 1%.

4.5.5 In some cases, composition of the test solution may change as a result of catalytic decomposition or by reaction with the test coupon. These changes should be determined if possible. Where required, the exhausted constituents should be added or a fresh solution provided, during the course of the test.

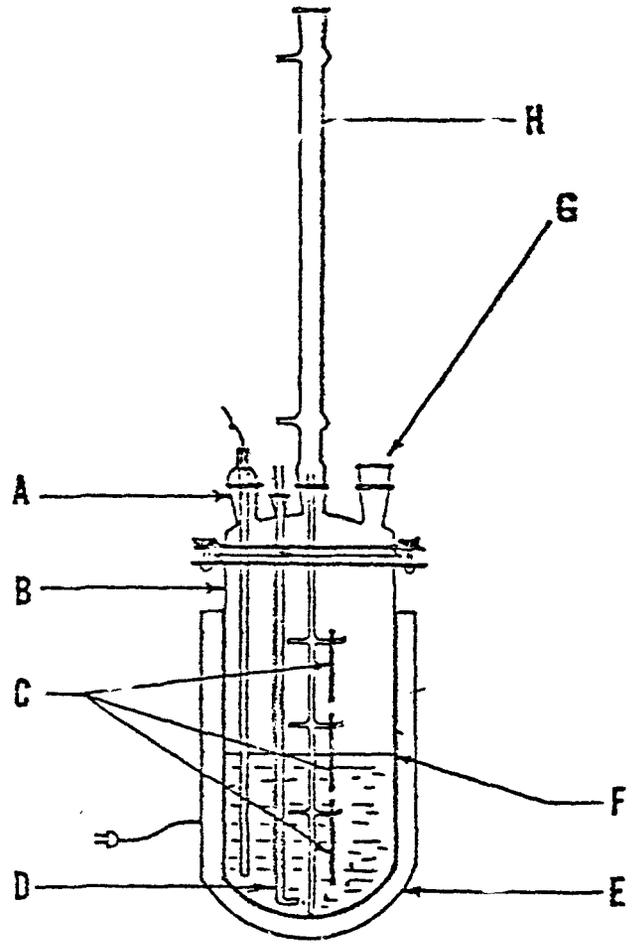


Figure 1 — Typical resin flask that can be used as a versatile and convenient apparatus to conduct simple immersion tests. Configuration of the flask top is such that more sophisticated apparatus can be added as required by the specific test being conducted. A = thermowell, B = resin flask, C = specimens 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.

4.5.6 When possible, only one type of metal should be exposed in a given test. If several different metals are exposed in the same solution, the corrosion products from one metal may affect the rate of attack on another metal. For example, copper corrosion products can reduce corrosion of stainless steel and titanium but can accelerate corrosion of aluminum.

4.6 Temperature of solution.

4.6.1 Temperature of the corroding solution should be controlled within ± 1 C (± 1.8 F) and must be stated in the report of test results.

4.6.2 If no specific temperature, such as boiling, is required or if a temperature range is to be investigated, the selected temperatures used in the test must be reported.

4.6.3 For tests at ambient temperatures, the tests should be conducted at the highest temperature anticipated for stagnant storage in summer months. This temperature may be as high as 40 to 45 C (104 to 113 F) in some areas. The variation in temperature should be reported also (e.g., 40 C ± 2 C).

4.7 Aeration of solution.

4.7.1 Unless specified, the solution should not be aerated. Most tests related to process equipment should be run with the natural atmosphere inherent in the process, such as the vapors of the boiling liquid.

4.7.2 If aeration is used, the specimens should not be located in the direct air stream from the sparger. Extraneous effects can be encountered if the air stream impinges on the specimens.

4.7.3 If complete exclusion of dissolved oxygen is necessary, specific techniques are required such as prior heating of the solution and sparging with an inert gas (usually nitrogen). A liquid atmospheric seal is required on the test vessel to prevent further contamination.

4.7.4 If oxygen saturation of the test solution is desired, this can best be achieved by sparging. For other degrees of aeration, the solution should be sparged with synthetic mixtures of air or oxygen with an inert gas.

4.8 Solution velocity

4.8.1 The effect of velocity is not usually determined in normal laboratory tests although specific tests have been designed for this purpose. However, for the sake of reproducibility, some velocity control is desirable.

4.8.2 Tests at the boiling point should be conducted with minimum possible heat input, and boiling chips should be used to avoid excessive turbulence and bubble impingement.

4.8.3 In tests conducted below the boiling point, thermal convection generally is the only source of liquid velocity.

.4 In test solutions with high viscosities, supplemental controlled stirring is recommended.

4.9 Volume of test solution.

4.9.1 The volume of the test solution should be large enough to avoid any appreciable change in its corrosiveness either through exhaustion of corrosive constituents or accumulation of corrosion products that might affect further corrosion. 5.3-13

4.9.2 The preferred minimum volume-to-area ratio is 250 milliliters of solution per square inch of specimen surface as stipulated in ASTM Standard A-279-63 on "Total Immersion Corrosion Test of Stainless Steels."

4.9.3 When the test objective is to determine the effect of a metal or alloy on the characteristics of the test solution (for example, to determine the effects of metals on dyes), it is desirable to reproduce the ratio of solution volume to exposed metal surface that exists in practice. The actual time of contact of the metal with the solution also must be taken into account. Any necessary distortion of the test conditions must be considered when interpreting the results.

4.10 Method of supporting specimens.

4.10.1 The supporting device and container should not be affected by or cause contamination of the test solution.

4.10.2 The method of supporting specimens will vary with the apparatus used for conducting the test but should be designed to insulate the specimens from each other physically and electrically and to insulate the specimens from any metallic container or supporting device used with the apparatus.

4.10.3 Shape and form of the specimen support should assure free contact of the specimen with the corroding solution, the liquid line, or the vapor phase as shown in Figure 1. If clad alloys are exposed, special procedures will be required to insure that only the cladding is exposed unless the purpose is to test the ability of the cladding to protect cut edges in the test solution.

4.10.4 Some common supports are glass or ceramic rods, glass saddles, glass hooks, fluorocarbon plastic strings, and various insulated or coated metallic supports.

4.11 Duration of test.

4.11.1 Although duration of any test will be determined by the nature and purpose of the test, an

excellent procedure for evaluating the effect of time on corrosion of the metal and also on the corrosiveness of the environment in laboratory tests has been presented by Wachter and Treseder.[2] This technique is called the "Planned Interval Test," and the procedure and evaluation of results are given in Table 1. Other procedures that require the removal of solid corrosion products between exposure periods will not measure accurately the normal changes of corrosion with time.

4.11.2 Materials which experience severe corrosion generally do not need lengthy tests to obtain accurate corrosion rates. Although this assumption is valid in many cases, there are cases where it is not valid. For example, lead exposed to sulfuric acid corrodes at an extremely high rate at first while building a protective film, then the rates decrease considerably so that further corrosion is negligible. The phenomenon of forming a protective film is observed with many corrosion resistant materials, and therefore short tests on such materials would indicate a high corrosion rate and would be completely misleading.

4.11.3 Short time tests also can give misleading results on alloys that form passive films, such as stainless steels. With borderline conditions, a prolonged test may be needed to permit breakdown of the passive film and subsequently more rapid attack. Consequently, tests run for long periods are considerably more realistic than those conducted for short durations. This statement must be qualified by stating that corrosion should not proceed to the point where the original specimen size or the exposed area is drastically reduced or where the metal is perforated.

4.11.4 If anticipated corrosion rates are moderate or low the following equation[2] gives a suggested test duration:

$$\text{Duration of test (hr)} = \frac{2000}{\text{corrosion rate (mpy)}}$$

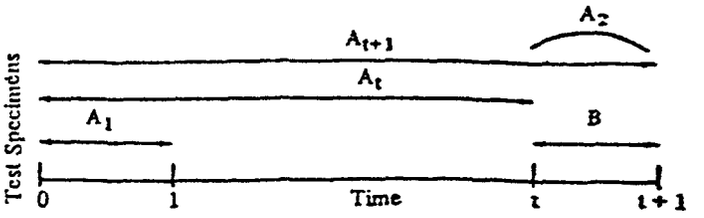
Examples: Where the corrosion rate is 10 mpy, the test should run for at least 200 hours. If the rate is 1 mpy, the duration should be at least 2000 hours.

4.11.4.1 This method of estimating test duration is useful only as an aid in deciding, after a test has been made, whether or not it is desirable to repeat the test for a longer period. The most common testing periods are 48 to 168 hours (2 to 7 days).

4.11.5 In some cases, it may be necessary to know the degree of contamination caused by the products of corrosion; this can be accomplished by analysis of

TABLE 1 — Planned Interval Test[2]

(Reprinted by permission from "Chemical Engineering Progress," June, 1947.)



Identical specimens-all placed in the same corrosive fluid. Imposed conditions of the test kept constant for entire time t + 1. Letters, A_1, A_t, A_{t+1}, B, represent corrosion damage experienced by each test specimen. A_2 is calculated by subtracting A_t from A_{t+1}.

Occurrences During Corrosion Test		Criteria
Liquid corrosiveness	unchanged	$A_1 = B$
	decreased	$B < A_1$
	increased	$A_1 < B$
Metal corrodibility	unchanged	$A_2 = B$
	decreased	$A_2 < B$
	increased	$B < A_2$

Combinations of Situations

Liquid Corrosiveness	Metal Corrodibility	Criteria
1. unchanged	unchanged	$A_1 = A_2 = B$
2. unchanged	decreased	$A_2 < A_1 = B$
3. unchanged	increased	$A_1 = B < A_2$
4. decreased	unchanged	$A_2 = B < A_1$
5. decreased	decreased	$A_2 < B < A_1$
6. decreased	increased	$A_1 > B < A_2$
7. increased	unchanged	$A_1 < A_2 = B$
8. increased	decreased	$A_1 < B > A_2$
9. increased	increased	$A_1 < B < A_2$

Example of Planned Interval Corrosion Test

Conditions: Duplicate strips of low-carbon steel, each 3/4 by 3 in., immersed in 200 ml of 10% $AlCl_3$ - 90% $SbCl_3$ mixture through which dried HCl gas was slowly bubbled at atm. pressure. Temperature 90 C.

	Interval, days	Wt. Loss, mg	Penetration, mils	Apparent Corrosion Rate, mils/yr
A_1	0-1	1080	1.69	620
A_t	0-3	1430	2.24	270
A_{t+1}	0-4	1460	2.29	210
B	3-4	70	0.11	40
A_2	calc. 3-4	30	0.05	18

$A_2 < B < A_1$
$0.05 < 0.11 < 1.69$

Therefore, liquid markedly decreased in corrosiveness during test, and formation of partially protective scale on the steel was indicated.

the solution after corrosion has occurred. The corrosion rate can be calculated from the concentration of the matrix metal found in the solution, and it can be compared to that determined from the weight loss of the specimens. However, some of the corrosion products usually adhere to the specimen as a scale, and the corrosion rate calculated from the metal content in the solution is not always correct.

5. Methods of Cleaning Specimens After the Test

5.1 Before specimens are cleaned, their appearance should be observed and recorded. Location of deposits, variations in types of deposits, or variations in corrosion products are extremely important in evaluating localized corrosion, such as pitting and concentration cell attack.

5.2 Cleaning specimens after the test is a vital step in the corrosion test procedure and, if not done properly, can cause misleading results.

5.2.1 Generally, the cleaning procedure should

TABLE 2—Methods for Chemical Cleaning of Corrosion Test Specimens After Exposure

Material	Chemical	Time	Temperature	Remarks
Aluminum and Aluminum Alloys	70% HNO_3	2-3 min	Room	Follow by light scrub.
	or			
	2% CrO_3, 5% H_3PO_4, Soln.	10 min	175-185 F (79-85 C)	Used when oxide film resists HNO_3 treatment. Follow by 70% HNO_3 treatment previously described.
Copper and Copper Alloys	15-20% HCl	2-3 min	Room	Follow by light scrub.
	or			
	5-10% H_2SO_4	2-3 min	Room	Follow by light scrub.
Lead and Lead Alloys	1% acetic acid	10 min	Boiling	Follow by light scrub. Removes PbO.
	or			
	5% ammonium acetate	5 min	Hot	Follow by light scrub. Removes PbO and/or $PbSO_4$.
	or			
	80 g/l NaOH, 50 g/l mannitol, 0.62 g/l hydrazine sulfate	30 min, or until clean	Boiling	Follow by light scrub.
Iron and Steel	20% NaOH, 200 g/l zinc dust	5 min	Boiling	---
	or			
	conc. HCl, 50 g/l, $SnCl_2$ + 20 g/l $SbCl_3$	Until clean	Cold	---
Magnesium and Magnesium Alloys	15% CrO_3, 1% $AgCrO_4$ Soln.	15 min	Boiling	---
Nickel and Nickel Alloys	15-20% HCl	Until clean	Room	---
	or			
	10% H_2SO_4	Until clean	Room	---
Stainless Steel	10% HNO_3	Until clean	140 F (60 C)	Avoid contamination with chlorides
Tin and Tin Alloys	15% Na_3PO_4	10 min	Boiling	Follow by scrubbing.
Zinc	10% NH_4Cl followed by 5% CrO_3, 1% $AgNO_3$ Soln.	5 min 20 sec	Room Boiling	Follow by light scrubbing.
	or			
	Saturated ammonium acetate	Until clean	Room	Follow by light scrub.
	or			
	100 g/l NaCN	15 min	Room	---

remove all corrosion products from specimens with a minimum removal of sound metal.

5.2.2 Set rules cannot be applied to specimen cleaning because procedures will vary depending on the type of metal being cleaned and on the degree of adherence of corrosion products.

5.3 Cleaning methods can be divided into three general categories: mechanical, chemical, and electrolytic.

5.3.1 Mechanical cleaning includes scrubbing, scraping, brushing, mechanical shocking, and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods; the others are used principally as a supplement to remove heavily encrusted corrosion products before scrubbing. Care should be used to avoid the removal of sound metal.

5.3.2 Chemical cleaning implies the removal of material from the surface of the specimen by dissolution in an appropriate chemical solution. Solvents such as acetone, carbon tetrachloride, and alcohol, are used to remove oil, grease, or resin and are usually applied prior to other methods of cleaning. Chemicals are chosen for application to a specific material. Some of these treatments in general use are outlined in Table 2.

5.3.3 Electrolytic cleaning should be preceded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that has been found to be useful for many metals and alloys is as follows:

Solution	5% (by weight) H_2SO_4
Anode	Carbon or lead
Cathode	Test specimen.
Cathode C.D.	20 amp/dm² (129 amp/sq in)
Inhibitor	2 cc organic inhibitor per liter
Temperature	74 C (165 F)
Exposure period	3 minutes

5.3.3.1 Precautions must be taken to insure good electrical contact with the specimen, to avoid contamination of the solution with easily reducible metal ions, and to insure that inhibitor decomposition has not occurred. Instead of using 2 milliliters of any proprietary inhibitor, 0.5 gram per liter of inhibitors such as diorthotolyl thiourea or quinoline ethiodide can be used.

5.4 Whatever treatment is used to clean specimens after a corrosion test, its effect in removing metal should be determined, and the weight loss should be corrected accordingly. A "blank" specimen should be weighed before and after exposure to the cleaning procedure to establish this weight loss.

5.4.1 Following removal of all scale, the specimen should be treated as discussed in Section 2.8.

5.4.2 A description of the cleaning method should be included with the data reported.

6. Evaluation of Results

6.1 After corroded specimens have been cleaned, they should be reweighed with an accuracy corresponding to that of the original weighing. The weight loss during the test period can be used as the principal measure of corrosion.

6.2 After the specimens have been reweighed, they should be examined carefully for the presence of pits. If there are pits, the average and maximum depths of pits are determined after measurement with a pit gauge or a calibrated microscope which can be focused first on the edge and then on the bottom of the pit. An excellent discussion of pitting corrosion has been published.[3]

6.2.1 Pit depths should be reported in millimeters or thousandths of an inch for the test period and not interpolated or extrapolated to millimeters per year or thousandths of an inch per year or any other arbitrary period because rarely, if ever, is the rate of initiation or propagation of pits uniform.

6.2.2 The size, shape, and distribution of pits should be noted. A distinction should be made between those occurring underneath the supporting devices (concentration cells) and those on surfaces that were freely exposed to the test solution.

6.3 If the material being tested is suspected of being subject to dealloying forms of corrosion such as dezincification, or to intergranular attack, a cross section of the specimen should be microscopically examined to determine the type and depth of such attack.

6.4 The specimen may be subjected to simple bending tests to determine whether any embrittlement has occurred.

6.5 It may be desirable to make quantitative mechanical tests to compare the exposed specimens with uncorroded specimens reserved for the purpose, as described in Section 2.2.

7. Calculating Corrosion Rates

5.3-17

7.1 The calculation of corrosion rates requires several pieces of information and several assumptions.

7.1.1 The use of corrosion rates implies that all weight loss has been due to general corrosion and not to localized corrosion, such as pitting or sensitized areas on welded coupons. Localized corrosion is reported separately.

7.1.2 The use of corrosion rates also implies that the material has not been internally attacked as by dezincification or intergranular corrosion.

7.1.3 Internal attack can be expressed as a corrosion rate if desired. However, the calculations must not be based on weight loss, which is usually small, but on microsections which show depth of attack.

7.2 Assuming that localized or internal corrosion is not present or are recorded separately in the report, the corrosion rate expressed as mils penetration per year (mpy) or millimeters per year (mmpy) can be calculated by the equations:

$$\text{mpy} = \frac{\text{wt loss} \times 534}{(\text{area})(\text{time})(\text{metal density})}$$

$$\text{mmpy} = \frac{\text{wt loss} \times 13.56}{(\text{area})(\text{time})(\text{metal density})}$$

where weight loss is in milligrams, area is square inches of metal surface exposed, and time is hours exposed.

Metal density of many common alloys (expressed in grams per cubic centimeter) is listed in Table 3. The density for new or unlisted alloys can be obtained from the producer or from various metal handbooks.

TABLE 3 — Density of Common Metals for Use in Corrosion Rate Calculations[9]

Alloy	Density, g/cc
Aluminum	
99.0 + Al	2.71
Al, 1.2 Mn	2.73
Al, 1.0 Mg, 0.6 Si, 0.25 Cr	2.70
Brass	
85 Cu, 15 Zn	8.75
71 Cu, 28 Zn, 1 Sn	8.53
65 Cu, 35 Zn	8.47
60 Cu, 39.25 Zn, 0.75 Sn	8.41
Bronze	
95 Cu, 5 Sn	8.86
90 Cu, 10 Sn	8.78
85 Cu, 5 Sn, 5 Zn, 5 Pb	8.80
94.8 Cu, 3 Si	8.53
95 Cu, 5 Al	8.17
85-90 Cu, 10 Al	7.58
Copper	
99.90 Cu, 0.01 P	8.91
Cupro-Nickel	
90 Cu, 10 Ni	8.93
70 Cu, 30 Ni	8.94
Iron	
94 Fe, 3.5 C, 2.5 Si	7.00
96 Fe, 3.0 C	7.60
99 Fe, 0.025 S, 0.017 Mn, 0.012 C, 0.005 P	7.86
14.5 Si, 0.35 Mn, 0.85 C	7.00
Lead	
99.90 + Pb	11.34
Nickel	
99.4 Ni + Co	8.89
67 Ni, 30 Cu	8.84
62 Ni, 30 Mo, 5 Fe	9.24
58 Ni, 17 Mo, 15 Cr, 5 W, 5 Fe	8.94
80 Ni, 14 Cr, 6 Fe	8.51
Steel	
0.20 C, Mn, P, S	7.85
Stainless Steel	
11.50-13.50 Cr, 0.15 C	7.75
14.00-18.00 Cr, 0.12 C	7.70
18.00-20.00 Cr, 8.00-12.00 Ni, 0.08 C	7.93
16.00-18.00 Cr, 10.00-14.00 Ni, 2.00-3.00 Mo, 0.08 C	7.98
17.00-19.00 Cr, 9.00-12.00 Ni, 0.08 C, Ti	8.02
17.00-19.00 Cr, 9.00-12.00 Ni, 0.08 C, Cb	8.02
19.00-21.00 Cr, 24.00-30.00 Ni, 2.00-3.00 Mo, 3.00-4.00 Cu	8.02
Tantalum	16.60
Tin	7.30
Titanium	4.54
Zirconium	6.53

8. Reporting the Data

8.1 The importance of reporting all data as completely as possible cannot be overemphasized.

8.2 Expansion of the testing program in the future or correlating the results with tests of other investigators will be possible only if all pertinent information is properly recorded.

8.3 The following checklist is a recommended guide for reporting all important information and data:

8.3.1 Corrosive media and concentration (changes during test).

8.3.2 Volume of test solution.

8.3.3 Temperature (maximum, minimum, average).

8.3.4 Aeration (describe conditions or technique).

8.3.5 Agitation (describe conditions or technique).

8.3.6 Type of apparatus used for test.

8.3.7 Duration of each test.

8.3.8 Chemical composition or trade name of metals tested.

8.3.9 Form and metallurgical conditions of specimens.

8.3.10 Exact size, shape, and area of specimens.

8.3.11 Treatment used to prepare specimens for test.

8.3.12 Number of specimens of each material tested, and whether specimens were tested separately or which specimens were tested in the same container.

8.3.13 Method used to clean specimens after exposure and the extent of any error expected by this treatment.

8.3.14 Actual weight losses for each specimen.

8.3.15 Evaluation of attack if other than general, such as crevice corrosion under support rod, pit depth and distribution, and results of microscopic examination or bend tests.

8.3.16 Corrosion rates for each specimen expressed as mils per year.

8.4 Minor occurrences or deviations from the proposed test program often can have significant effects and should be reported if known.

8.5 Statistics can be a valuable tool for analyzing the results from test programs designed to generate adequate data and should be used wherever possible. Excellent references for the use of statistics in corrosion studies include References 4 through 8.

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Membership of Unit Committee T-5A

Section 6.0

REACTIVITY

Introduction

The regulation (40 CFR 261.23) defines reactive wastes to include wastes which (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.

Sub-Section 6.1

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.
6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.
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.

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.

Sub-Section 6.2

DEFINITION OF EXPLOSIVE MATERIALS

For purposes of this regulation a waste which is a reactive waste by reason of explosivity is one which 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, and 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 fireworks 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. 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.

11. 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.

12. 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, ureanitrate, pentolite, commercial boosters.

13. 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.

14. 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.

15. 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.

16. 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.

17. Detonating primers which contain a detonator and an additional charge of explosives, all assembled in a suitable envelope.

18. 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 classed as class C explosives and are not reactive waste.

19. 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.

20. 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.

21. 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.

22. Explosive bombs. Explosive bombs are metal or other containers filled with explosives. They are used in warfare and include airplane bombs and depth bombs.

23. Explosive mines. Explosive mines are metal or composition containers filled with a high explosive.

24. Explosive torpedoes. Explosive torpedoes, such as those used in warfare, are metal devices containing a means of propulsion and a quantity of high explosives.

25. 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.

26. 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 by utilized to project chemicals.

27. 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.

28. Jet thrust units or other rocket motors containing a mixture of chemicals capable of burning rapidly and producing considerable pressure.

29. Propellant mixtures (i.e, and 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 inches in diameter and 4 inches 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 percent mercury fulminate and 20 percent 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-pound weight may be dropped from predetermined heights so as to impact specific quantities of liquid or solid materials under fixed conditions. Detailed prints may be obtained from the Bureau of Explosives, 2 Pennsylvania Plaza, New York, New York, 10001.

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.

Section 7.0

EXTRACTION PROCEDURE TOXICITY

Introduction

The Extraction Procedure (EP) is designed to simulate the leaching a waste will undergo if disposed of in an improperly designed sanitary landfill. It is a laboratory test in which a representative sample of a waste is extracted with distilled water maintained at pH = 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 8 elements (i.e., arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver), four pesticides (i.e., Endrin, Lindane, Methoxychlor, Toxaphene), and two herbicides (i.e., 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.

The Extraction Procedure consists of 5 steps:

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 either pass through a 9.5 mm (0.375 in) standard sieve, have a surface area per gram of waste of 3.1 cm^2, 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 hours in an aqueous medium whose pH is maintained at or below 5, using 0.5 N acetic acid. The pH is maintained either automaticlly or manually. Acidification to ph 5 is subject to a specification as to total amount of acid to be added to the system.

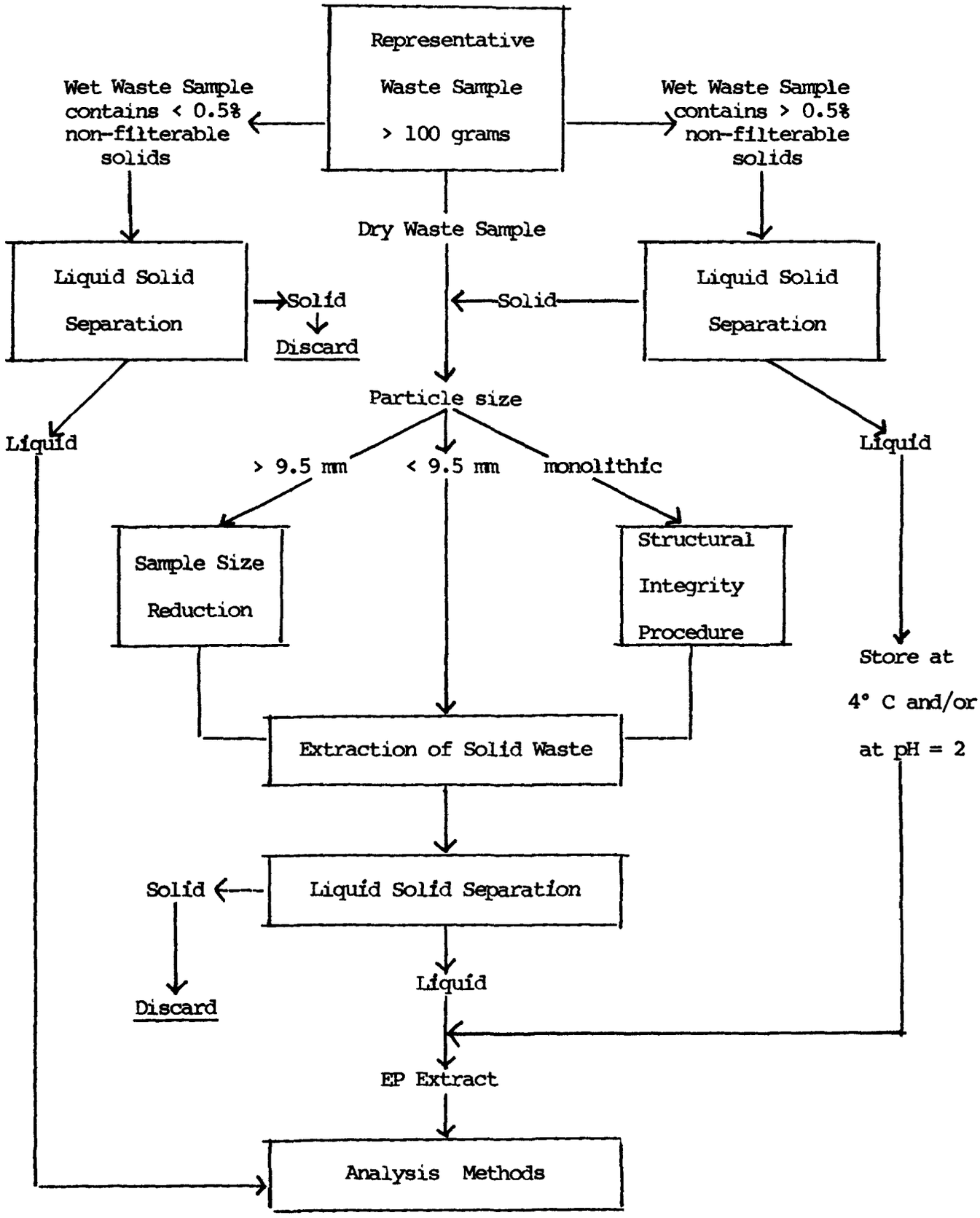
4. Final Separation of the Extraction from the Remaining Solid

After extraction, the liquid: solid ratio is adjusted to 20:1 and the mixture of solid and extraction liquid are separated by filtration, the solid discarded and the liquid combined with the filtrate obtained in step 1. This is the EP Extract that is subjected to the evaluation requirements in 40 CFR 261.24.

5. Testing (Analysis) of EP Extract

Inorganic and organic species are identified and quantified using the appropriate methods in Section 8 of this manual.

Figure 7.0
EXTRACTION PROCEDURE FLOWCHART



Sub-Section 7.1

CHARACTERISTIC OF EP TOXICITY REGULATION

A solid waste exhibits the characteristic of EP toxicity if, using the test methods described in Appendix II of 40 CFR Part 261 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 7.1-1 at a concentration equal to or greater than the respective value given in that Table. Where the waste contains less than 0.5 percent filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of this section.

A solid waste that exhibits the characteristic of EP toxicity, but is not listed as a hazardous waste in Subpart D, has the EPA Hazardous Waste Number specified in Table 7.1-1 which corresponds to the toxic contaminant causing it to be hazardous.

Table 7.1-1

MAXIMUM CONCENTRATION OF CONTAMINANTS
FOR CHARACTERISTIC OF EP TOXICITY

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (milligrams per liter)
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-dimethanonaphthalene	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 ($C_{10}H_{10}Cl_8$, Technical chlorinated camphene, 67-69 percent 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

APPENDIX II

EP TOXICITY TEST

Procedure

1. A representative sample of the waste to be tested (minimum size 100 grams) should be obtained using the methods specified in Appendix I of 40 CFR 261 or any other method capable of yielding a representative sample within the meaning of 40 CFR 260.
2. The sample should be separated into its component liquid and solid phases using the method described in "Separation Procedure" below. If the dry weight of the solid residue* obtained using this method totals less than 0.5% of the original wet weight of the waste, the residue can be discarded and the operator should treat the liquid phase as the extract and proceed immediately to Step 8.
3. The solid material obtained from the Separation Procedure should be evaluated for its particle size. If the solid material has a surface area per gram of material equal to, or greater than, 3.1 cm^2 or passes through a 9.5 mm (0.375 inch) standard sieve, the operator should proceed to Step 4. If the surface area is smaller or the

*The percent solids is determined by drying the filter pad at 80°C until it reaches constant weight and then calculating the percent solids using the following equation:

$$\frac{\text{(weight of pad + solid) - (tare weight of pad)}}{\text{initial wet weight of sample}} \times 100 = \% \text{ solids}$$

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 inch) sieve or, if the material is in a single piece, by subjecting the material to the "Structural Integrity Procedure" described below.

4. The solid material obtained in Step 3 should be weighed immediately and placed in an extractor with 16 times its weight of deionized water. Do not allow the material to dry prior to weighing. For purposes of this test, an acceptable extractor is one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also insure that all sample surfaces are continuously brought into contact with well mixed extraction fluid.

5. 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, 0.5N 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 hours and maintained at 20°-40°C (68° 104°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 0.5N acetic acid. If such a system is not available, the following manual procedure shall be employed:

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

b. The pH of the solution should be checked and, if necessary, 0.5N 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 minute intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5 pH units.

c. The adjustment procedure should be continued for at least 6 hours.

d. If at the end of the 24-hour 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 four hours, during which the pH should be adjusted at one hour intervals.

6. At the end of the 24 hour extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

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

V= ml deionized water to be added

W= weight in grams of solid charged to extractor

A= ml of 0.5N acetic acid added during extraction

7. The material in the extractor should be separated into its component liquid and solid phases as described under "Separation Procedure."

8. The liquids resulting from Steps 2 and 7 should be combined. This combined liquid (or the waste itself if it has less than 0.5% solids, as noted in step 2) is the extract and should be analyzed for the presence of any of the contaminants specified in Table I of 40 CFR 261.24 using the Analytical Procedures designated below.

Separation Procedure

Apparatus

A filter holder, designed for filtration media having a nominal pore size of 0.45 micrometer and capable of applying a 5.3 kg/cm^2 (75 psig) hydrostatic pressure to the solution being filtered shall be used. For mixtures containing non-absorptive solids, where separation can be effected without imposing a 5.3 kg/cm^2 pressure differential, vacuum filters employing a 0.45 micrometer filter media can be used.

Procedure*

1. Following manufacturer's directions, the filter unit should be assembled with a filter bed consisting of a 0.45 micrometer filter membrane. For difficult or slow to filter mixtures a prefilter bed consisting of the following prefilters in increasing pore size (0.65 micrometer membrane, fine glass fiber prefilter, and coarse glass fiber prefilter) can be used.
2. The waste should be poured into the filtration unit.
3. The reservoir should be slowly pressurized until liquid begins to flow from the filtrate outlet at which point the pressure in the filter should be immediately lowered to 10-15 psig. Filtration should be continued until liquid flow ceases.
4. The pressure should be increased stepwise in 10 psig increments to 75 psig and filtration continued until flow ceases or the pressurizing gas begins to exit from the filtrate outlet.

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*This procedure is intended to result in separation of the "free" liquid portion of the waste from any solid matter having a particle size >0.45um. If the sample will not filter, various other separation techniques can be used to aid in the filtration. As described above, pressure filtration is employed to speed up the filtration process. This does not alter the nature of the separation. If liquid does not separate during filtration, the waste can be centrifuged. If separation occurs during centrifugation, the liquid portion (centrifugate) is filtered through the 0.45um filter prior to becoming mixed with the liquid portion of the waste obtained from the initial filtration. Any material that will not pass through the filter after centrifugation is considered a solid and is extracted.

5. The filter unit should be depressurized, the solid material removed and weighed and then transferred to the extraction apparatus, or, in the case of final filtration prior to analysis, discarded. If the solid is to be extracted do not allow the material retained on the filter pad to dry prior to weighing.
6. The liquid phase should be stored at 4°C for subsequent use in Step 8.

Structural Integrity Procedure

Apparatus

A Structural Integrity Tester having a 3.18 cm (1.25 in.) diameter hammer weighing 0.33 kg (0.73 lbs.) 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 7-2.

Procedure

1. The sample holder should be filled with the material to be tested. If the sample of waste is a large monolithic block, a portion should be cut from the block having the dimensions of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) long cylinder. For a fixated waste, samples may be cast in the form of a 3.3 cm (1.3 in.) diameter x 7.1 cm (2.8 in.) cylinder for purposes of conducting this test. In such cases, the waste may be allowed to cure for 30 days prior to further testing.

2. The sample should be placed into the Structural Integrity Tester, then the hammer should be raised to its maximum height and dropped. This should be repeated fifteen times.
3. The material should be removed from the sample holder, weighed, and transferred to the extraction apparatus for extraction.

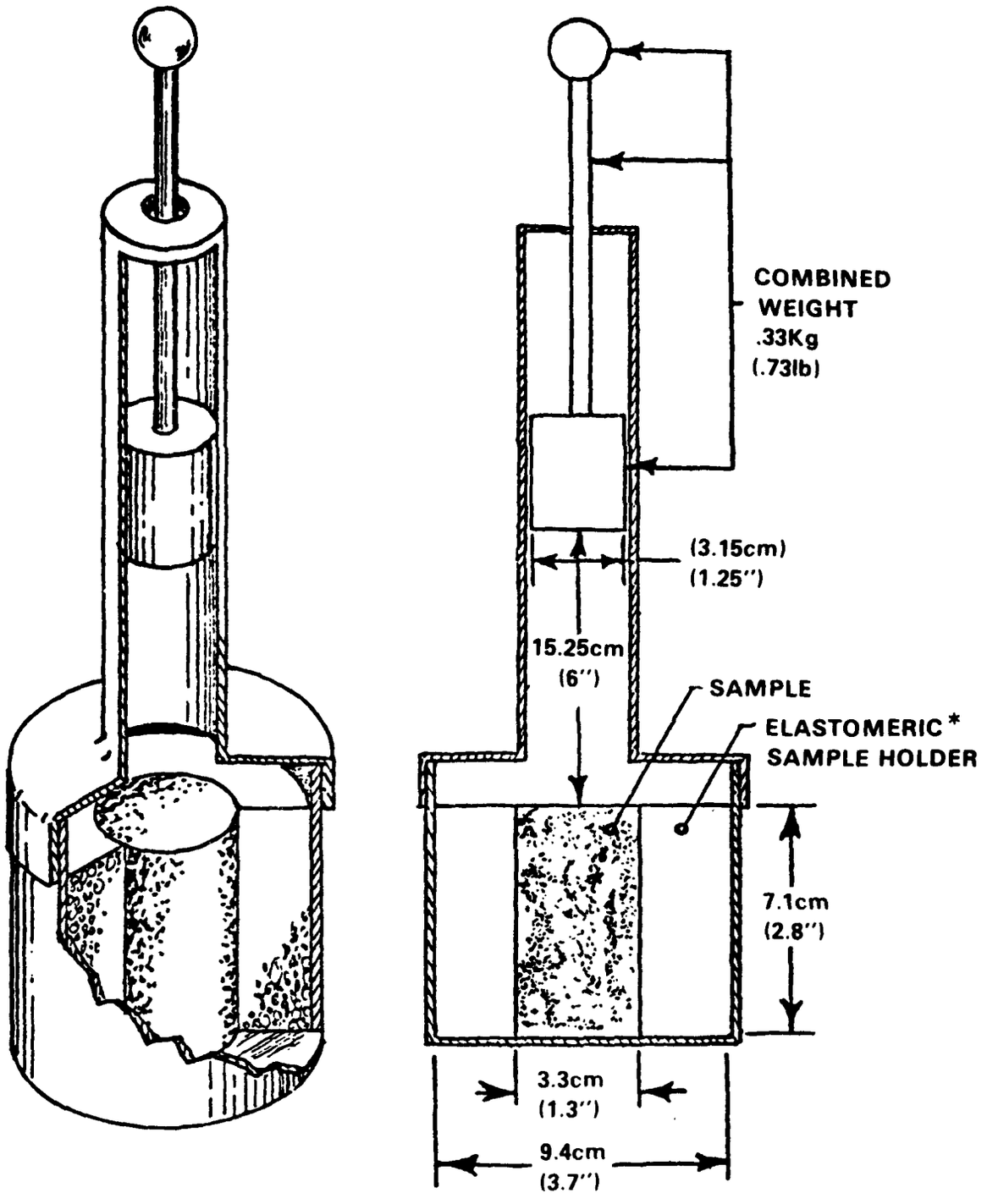
Procedures for Analyzing Extract

The test methods for analyzing the extract are as follows:

1. For arsenic, barium, cadmium, chromium, lead, mercury, selenium or silver: "Methods for Analysis of Water and Wastes," Environmental Monitoring and Support Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, Ohio 45268 (EPA-600/4-79-020, March 1979).
2. For Endrin; Lindane; Methoxychlor; Toxaphene; 2,4-D; 2,4,5-TP (Silvex): in "Methods for Benzidine, Chlorinated Organic Compounds, Pentachlorophenol and Pesticides in Water and Wastewater," September 1978, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.
   as standardized in "Test Methods for the Evaluation of Solid Waste, Physical/Chemical Methods."

For all analyses, the method of standard addition shall be used for the quantification of species concentration.

This method is described in "Test Methods for the Evaluation of Solid Waste." (It is also described in "Methods for Analysis of Water and Wastes.")



*ELASTOMERIC SAMPLE HOLDER FABRICATED OF MATERIAL FIRM ENOUGH TO SUPPORT THE SAMPLE

Figure 7.2

COMPACTION TESTER

Method 7.2

SEPARATION PROCEDURE

Scope and Application

This procedure is used to separate a waste into its liquid and solid phases both prior to and after extraction.

Summary of Method

The Separation Procedure involves vacuum or pressure filtration of a waste or extraction mixture. To minimize filtration time, pressure, settling, centrifugation and prefilters may be employed as an adjunct to filtration. Pressure filtration is required when vacuum filtration is inadequate for complete separation.

Apparatus

1. Filter holder: A filter holder capable of supporting a 0.45 um 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^2 (75 psi) of pressure. The type of filter holder used depends upon the properties of the mixture to be filtered. Filter holders known to the Agency and deemed suitable for use are listed in Table 7.2-1
2. Filter membrane: Filter membrane suitable for conducting the required filtration shall be fabricated from a material which:
   a. is not physically changed by the waste material to be filtered.
   b. does not absorb or leach the chemical species for which a waste's EP Extract will be analyzed.

Table 7.2-2 lists filter media known to the Agency and generally found to be suitable for solid waste testing.

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

   Use the following procedure to establish if a filter membrane will leach or adsorb chemical species.

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

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

   c. 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.

General Procedure

1. Weigh filter membrane and prefilter to $\pm$ 0.01 gram. Handle membrane and prefilters with blunt curved tip forceps or vacuum tweezers, or by applying suction with a pipette.

2. Assemble filter holder, membranes, and prefilters following the manufacturer's instructions. Place the 0.45 um membrane on the support screen and add prefilters in ascending order of pore size. Do not pre-wet filter membrane.

3. Allow slurries to stand to permit the solid phase to settle. Slow to settle wastes may be centrifuged prior to filtration.

4. 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.

5. Remove solid phase and filter media and weigh to $\pm$ 0.01 gram. Discard solid if it comprises less than 0.5% of the mixture (see below). If the sample contains >0.5% solids use the wet weight of the solid phase obtained in this separation for purposes of calculating amount of liquid and acid to employ for extraction using the following equation:

$$W = W_f - W_t$$

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

W_f = wet weight in grams of filtered solids and filter media

W_t = weight in grams of tared filters.

Procedure for Determining Percent Solids of a Waste

1. Determine percent solids of a waste sample by:
   a. separately weighing the waste sample and filters.
   b. filtering the waste material.
   c. drying the solid and filters at 80°C until two successive weighings yield the same value. Cal-

culate the percent solids using the following

equation:

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

NOTE: This procedure is only used to determine if the solid must be extracted or if 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 % solids determination is performed.

Table 7.2-1

APPROVED FILTER HOLDERS

Vacuum Filters

Manufacturer	Size	Model No.	Comments
Nalgene	500 ml	45-0045	Disposable plastic unit, includes prefilter and filter pads, and reservoir Should only be used when solution is to be analyzed for inorganic constituents
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	
Pressure Filters			
Nuclepore	142 mm	420800	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

Table 7.2-2

APPROVED FILTRATION MEDIA

Filter Type	Supplier	Filter To Be Used For Aqueous Systems*	Filter To Be Used For Organic Systems*
Coarse Prefilter	Gelman	61653 61669	61652 61669
	Nuclepore	210907 211707	210907 211707
	Millipore	AP25 042 00 AP25 127 50	AP25 042 00 AP25 127 00
Medium Prefilters	Nuclepore	21095 211705	21095 211705
	Millipore	AP20 042 00 AP20 124 50	AP20 042 00 AP20 124 50
Fine Prefilters	Nuclepore	210903 211703	210903 211703
	Millipore	AP25 042 00 AP25 127 50	AP25 042 00 AP25 127 50
Fine Filters (0.45um)	Gelman	60173 60177	60540 60544
	Pall	047NX50 142NX25	
	Nuclepore	111107 112007	181107 182007
	Millipore	HAWP 047 00 HAWP 142 50	FHLP 047 00 FHLP 142 00
	Selas	83485-02 83486-02	83485-02 83486-02

Method 7.4

STRUCTURAL INTEGRITY PROCEDURE

Application

The Structural Integrity Procedure (SIP) is employed to approximate the physical degradation a monolithic waste undergoes in a landfill or when compacted by earthmoving equipment.

Equipment

1. Structural Integrity Tester meeting the specifications detailed in Figure 7.4-1.
2. Sample holders of elastomeric material firm enough to support a cylindrical waste sample 3.3 cm (1.32 in.) in diameter and 7.1 cm (2.84 in.) long.

Procedure

1. Cut a 3.3 cm in diameter by 7.1 cm long cylinder from the waste material. For wastes which 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.
2. Place waste into sample holder and assemble the tester. Raise the hammer to its maximum height and drop. Repeat 14 times.
3. Remove solid material from tester and scrape off any particles adhering to sample holder. Weigh the waste to the nearest 0.01 gram and transfer its to the Extractor.

Sub-Section 7.5

EXTRACTORS

Introduction

An acceptable extractor is one which will prevent stratification of a waste sample and extraction fluid and will insure that all sample surfaces continuously contact well mixed extraction fluid. There are two types of acceptable extractors: 1) stirrers and 2) tumblers. Stirrers consist of a container in which the waste/extraction fluid mixture is agitated by spinning blades. Rotators agitate by turning a sample container end over end through a 360° revolution.

Stirrer

Scope and Application

One such stirrer approved for use in evaluating solid waste is illustrated in Figure 7.5-1. It is a container in which a waste/extraction fluid mixture is agitated by 2 blades spinning at $\geq$ 40 rpm. This extractor can be used with either automatic or manual pH adjustment.

Precautions

1. Large particles ($\geq$ 0.25 in. in diameter) may be ground by the spinning blades or abrade the container. If metal containers are employed this may result in contamination of the EP Extract.
2. Monolithic wastes should not be extracted in the stirrer as they may bend or break the stirring blades.

Summary of Operation

Place waste in extractor, add extraction fluid and stir for the required period of time. Adjust pH while stirrer is in operation by addition of acid through port in cover. pH may be continuously monitored using port in cover designed to accept a pH electorde.

Manufactures

Extractors of this design may be fabricated by the user or are known to be available commercially from Associated Design and Manufacturing Co. and Millipore Corporation.

Rotary Extractor

Scope and Application

The rotary extractor consists of a rack or box type device holding a number of plastic or glass bottles which rotate at approximately 29 rpm. Rotary extractors are used with manual pH adjustment.

Precautions

1. Use glass or fluorocarbon bottles for wastes whose EP Extract will be analyzed for organic compounds. For extracts to be analyzed only for metals, polyethylene bottles may be substituted.
2. Be careful not to tighten the screws too far and shatter the bottle when using the design in Figure 7.5-2.
3. Do not use glass bottles for extracting large blocks of waste as these may cause the bottles to shatter.

4. It is recommended that the bottles be alternated in an opposing manner in the apparatus to minimize torque (e.g., when one bottle faces up, the next bottle faces down.) When extracting an odd number of samples, balance the extractor by adding a bottle containing an amount of water approximately equal to the volume in the other bottles.

Equipment

1. Rotary extractors approved for use in evaulating the EP toxicity of solid wastes are illustrated in Figure 7.5-2 and 7.5-3.
2. Plastic or glass bottles sized to fit the particular extractor.
3. The equipment illustrated in Figure 7.5-2 may be fabricated by the user or is available commercially from Associated Design and Manufacturing Co.
4. The equipment illustrated in Figure 7.5-3 is available from the Acurex Corporation.

Summary of Operation

Fill plastic or glass bottles with the solid material. Add distilled deionized water to each bottle and start extractor. Stop extractor after 1 minute and adjust pH. Restart extractor and continue pH adjustment for the first six hours of agitation as described in the "Manual pH Adjustment Procedure" (Section 7.1). After 24 hours of agitation stop extractor, check pH as described and, if within range specified, adjust volume of fluid and remove for liquid solid separation.

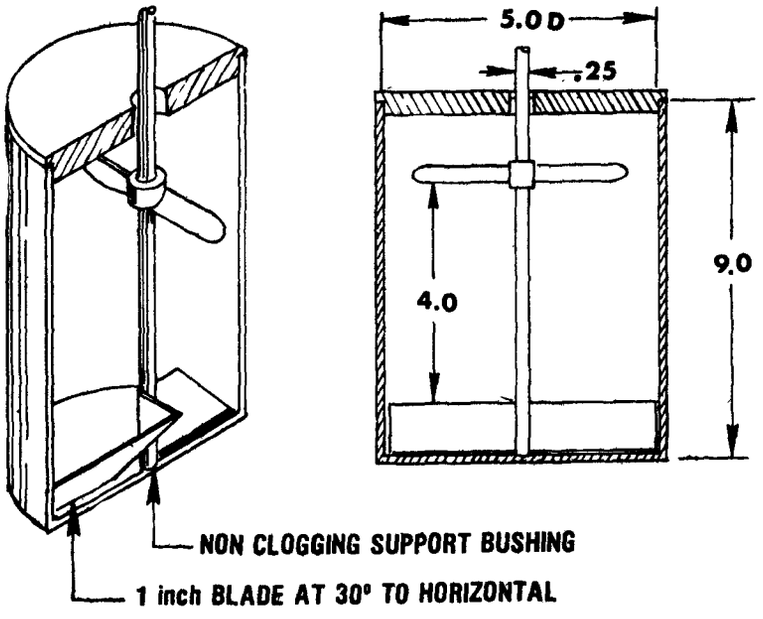


Figure 7.5-1
EXTRACTOR

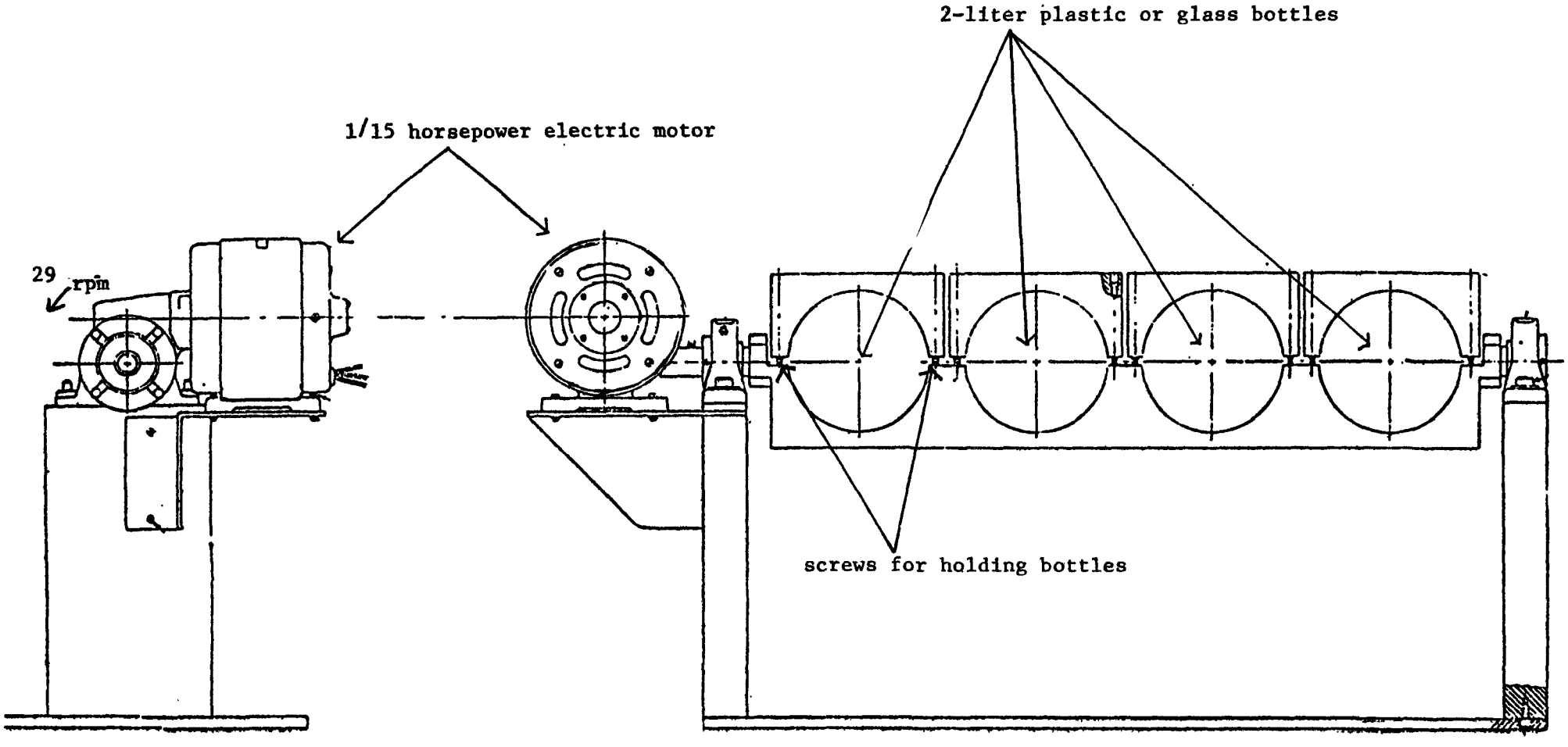


Figure 7.5-2
ROTARY EXTRACTOR

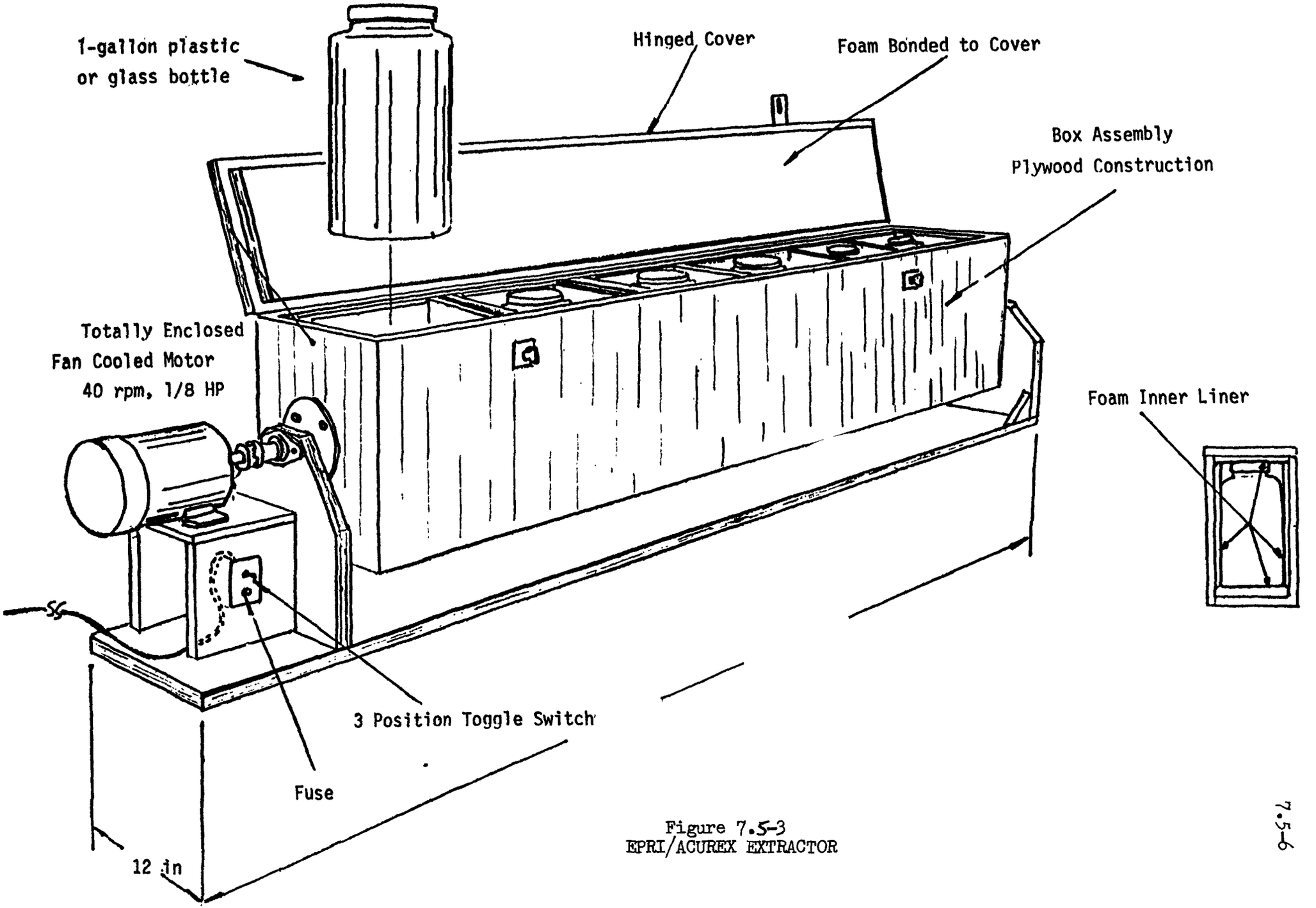


Figure 7.5-3
EPRI/ACUREX EXTRACTOR

Method 8.01

METHOD FOR VOLATILE ORGANICS

Scope and Application

The following volatile organic compounds may be determined by this method:

Volatile Compound	Detector
Acrylamide	FID
Benzyl Chloride	HSD
Bis(2-chloroethoxymethane)	HSD
Bis(2-Chloroisopropyl) ether	HSD
Carbon Disulfide	FID
Carbon Tetrachloride	HSD
Chloroacetaldehyde	HSD
Chlorobenzene	HSD, FID
Chloroform	HSD
Chloromethane	HSD
Dichlorobenzene	HSD
Dibromomethane	HSD
Ethyl ether	FID
Formaldehyde	FID
Methanol	FID
Methyl Ethyl Ketone	FID
Methyl Isobutyl Ketone	FID
Paraldehyde	FID
Tetrachloroethane	HSD
Tetrachloroethene	HSD
Trichloroethene	HSD
Trichlorofluoromethane	HSD
Trichloropropane	HSD
Vinyl Chloride	HSD
Vinylidene Chloride	HSD

Summary of Method

1. The volatile compounds are introduced to the gas chromatograph by direct injection (Method 8.80), the Headspace Method (Method 8.82), or the Purge and Trap method (Method 8.83). A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by either a halide specific detector (HSD) or a flame ionization dectector (FID). The detector used depends on the compound(s) of interest.
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.

Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A sample blank carried through sampling and subsequent storage and handling can serve as a check on such contamination.

Apparatus

1. Vial with cap - 40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105°C before use.
2. Septum - teflon - forced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C for one hour before use.

3. Sample introduction apparatus (Methods 8.80, 8.82 and 8.83)
4. Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories, including HSD or, FID, column supplies, recorder and gasses. A data system for measuring peak area is recommended.
5. Carbopack B 60/80 mesh coated with 1% SP-1000 packed in an 8 ft. x 0.1 in. ID stainless steel or glass column (Column 1) or Porisil-C 100/200 mesh coated with n-octane packed in a 6 ft. x 0.1 in. ID stainless steel or glass column (Column 2).
6. Syringes - 5 ml glass hypodermic with Luerlok tip (2 each).
7. Micro syringe - 10, 25, 100 ul.
8. 2-way syringe valve with Luer ends (3 each).
9. Syringe - 5 ml - gas tight with shut-off valve.
10. Bottle - 15 ml screw-cap, with teflon cap liner.

Reagents

1. Activated carbon - Filtrosorb 200 (Calspan Corp.) or equivalent.
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 minutes. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for one hour.

3. Stock standards - 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.

   a. Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

   b. Add the assayed reference material:

      i. Liquids

         Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

      ii. 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).

c. Reweigh, dilute to volume, stopper, then mix by by inverting the flask several times. Transfer the standard solution to a 15 ml screw cap bottle with a teflon cap liner.

d. Calculate the concentration in mg/l from the net gain in weight.

e. Store stock standards at 40° C. Prepare fresh standards weekly for the 4 compounds whose BP $\leq$ 30° C. All other standards must be replaced with fresh standards each month.

Calibration

1. Using stock standards, prepare secondary dilution standards in methyl alcohol that contains the compounds of interest, either singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in the Procedure section. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as detect $\leq$ 1 ug.

Quality Controls

1. Before processing any samples, the analyst should daily demonstrate through the analysis of an organic-free water or solvent blank that the entire analytical system is interference free.
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 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 chromatogam, confirmatory techniques such as mass spectroscopy should be used.

3. The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample with known amounts of the compounds the waste is being analyzed for. Using these spiked samples, readjust the sensitivity of the instrument such that 1 ug/gm of sample can be readily detected (see Quality Control).

Procedure

1. Assemble gas chromatograph with either Column 1 or 2. (See Apparatus section.)

   Column 1:

   a) Set helium gas flow at 40 ml/min flow rate.

   b) Set column temperature at 45° C for 3 minutes then program a 8° C/minute temperature rise to 220° C and hold for 15 minutes.

   Column 2:

   a) Set helium carrier gas flow at 40 ml/minute flow rate.

   b) Set column temperature at 50° C for 3 minutes, then

program a 6° C/min temperature rise to 170° C and hold for 4 minutes.

2. Introduce volatile compounds to the gas chromatograph using direct injection, headspace, or purge and trap.
3. Table 8.01-1 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 8.01-1.
4. Calibrate the system immediately prior to conducting any analysis and recheck as in Quality Control for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analyses session.

Calculations

1. If a response for the contaminant being analyzed for is greater than 2x background, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm of sample.

Table 8.01-1

ORGANOHALIDES TESTED USING PURGE AND TRAP METHOD

Compound	Retention Time (Min) Col. 1	Col. 2
Acrylamide		
Bis(2-chloroethoxymethane)		
Bis(2-chloroisopropyl) ether		
Carbon disulfide		
Carbon tetrachloride	13.0	14.4
Chloroacetaldehyde		
Chlorobenzene	24.2	18.8
Chloroform	10.7	12.1
Chloromethane	1.50	5.28
1,3-Dichlorobenzene	34.00	22.4
1,2-Dichlorobenzene	34.9	12.6
1,4-Dichlorobenzene	35.4	15.4
1,1-Dichloroethane	9.30	12.6
1,2-Dichloroethane	11.4	15.4
Dichloromethane		
Ethyl ether		
Formaldehyde		
Methanol		
Methyl ether ketone		
Methyl isobutyl ketone		
Paraldehyde (trimer of acetaldehyde)		

Compound	Retention Time (Min) Col. 1	Col. 2
1,1,2,2-Tetrachloroethane	21.6	--
1,2,2,2-Tetrachloroethane		
1,1,1,2-Tetrachloroethane		
Tetrachloroethene	21.7	15.0
1,1,1-Tetrachloroethane	12.6	13.1
1.1,2-Trichloroethane	16.5	18.7
Trichloroethene	15.8	13.1
Trichlorofluoromethane	7.18	
Trichloropropane		
Vinyl Chloride	2.67	5.28
Vinylidene Chloride		

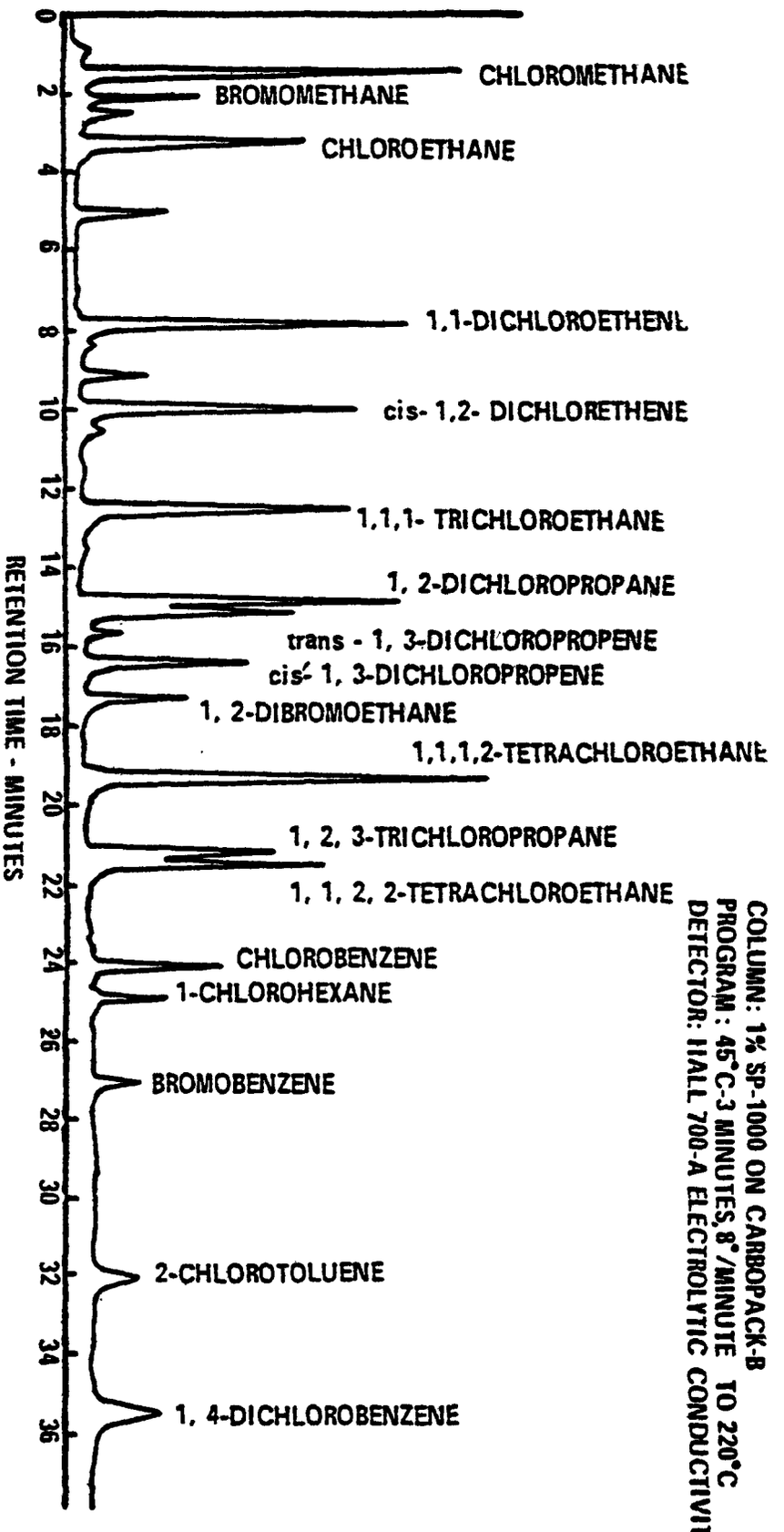


Figure 8.01-1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

Method 8.02

METHOD FOR VOLATILE AROMATICS, KETONES AND ETHERS

Scope and Application

This method covers the determination of certain volatile aromatics, some methyl ketones, and ethyl ether. The following compounds may be determined by this method:

Benzene

Chlorobenzene

Dichlorobenzene

Ethyl ether

Methyl ethyl ketone

Methyl isobutyl ketone

Toluene

Xylene

Summary of Method

The volatile compounds are introduced to the gas chromatograph by direct injection (Method 8.80), the headspace method (Method 8.82), or the purge and trap technique (Method 8.83). A temperature program is used in the GC system to separate the compounds prior to detection with a photoionization detector (PID) or flame ionization detector (FID).

Interferences

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorcarbons and methylene chloride) through the sample container septum during shipment and storage. A sample blank carried through sampling and subsequent storage and handling can serve as a check for such contamination.

Apparatus

1. Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including Model PI-51-02 photo-ionization detector (PID), column supplies, recorder and gases. A data system for measuring peak areas is recommended.
2. Supelcoport 100/200 mesh coated with 5% SP-2100 and 1.75% Bentone 34 packed in a 6 ft. x 0.085 inch ID stainless steel column.
3. Syringes - 5 ml glass hypodermic with Luerlok tip (2 each).
4. Micro syringes - 10, 25, 100 ul.
5. 2-way syringe valve with Luer ends (3 each).
6. Syringe - 5 ml gas-tight with shut-off valve.
7. Bottle - 15 ml screw-cap, with teflon cap liner.

Reagents

1. Activated carbon - Filtrosorb 200 (Calgon Corp.) or equivalent.
2. Organic-free water generated by passing distilled or deionized water through a filter bed containing of activated carbon. A water purification system (Millipore Super-Q or equivalent) may be used to generated organic-free deionized water. Organic free water may also be prepared by boiling water for 15 minutes. Subsequently while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour.

3. Stock standards - Prepare stock standard solution in methyl alcohol using assayed liquids. Because of the toxicity of many of the compounds being analyzed primary diluting 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.

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

   b. Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

   c. Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a teflon cap liner.

   d. Calculate the concentration in ug/ml from the net gain in weight.

   e. Store stock standards at 4°C. All standards must be replaced with fresh standard each month.

Calibration

1. Using stock standards, prepare secondary dilution standards in methyl alcohol that contains the compounds of interest, either singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in the Procedure section. By injecting secondary standards adjust the sensitivity limit and the linear range of the analytical system for each compound being analyzed for to a sensitivity of $\leq$ 1 ug/l (2 x background).

Quality Control

1. Before processing any samples the analyst should daily demonstrate through the analysis of an organic-free water or solvent blank that the entire analytical system is interference free.
2. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy and sensitivity of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.
3. The analysis should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample

matrix by spiking each sample with known amounts of the compounds the waste is being analyzed for. Using these spiked samples readjust the sensitivity of the instrument such that 1 ug/gm of sample can be readily detected.

Procedure

1. Assemble gas chromatograph with column specified in Apparatus section and detector indicated in Table 8.02-1.
2. Set helium carrier gas at 36 ml/min flow rate.
3. Hold column temperature at 50°C for 2 minutes then program a 6°C/minute rise to 90°/C for a final hold of 40 minutes.
4. Table 8.02-1 summarizes the estimated retention times for a number of organic compounds analyzable using this method. An example of the separation achieved by this column is shown in Figure 8.02-1.
5. Calibrate the system immediately prior to conducting any analyses and recheck as in Quality Control for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session.

Calculations

1. If a response for the contaminant being analyzed for is greater than 2 x background, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample

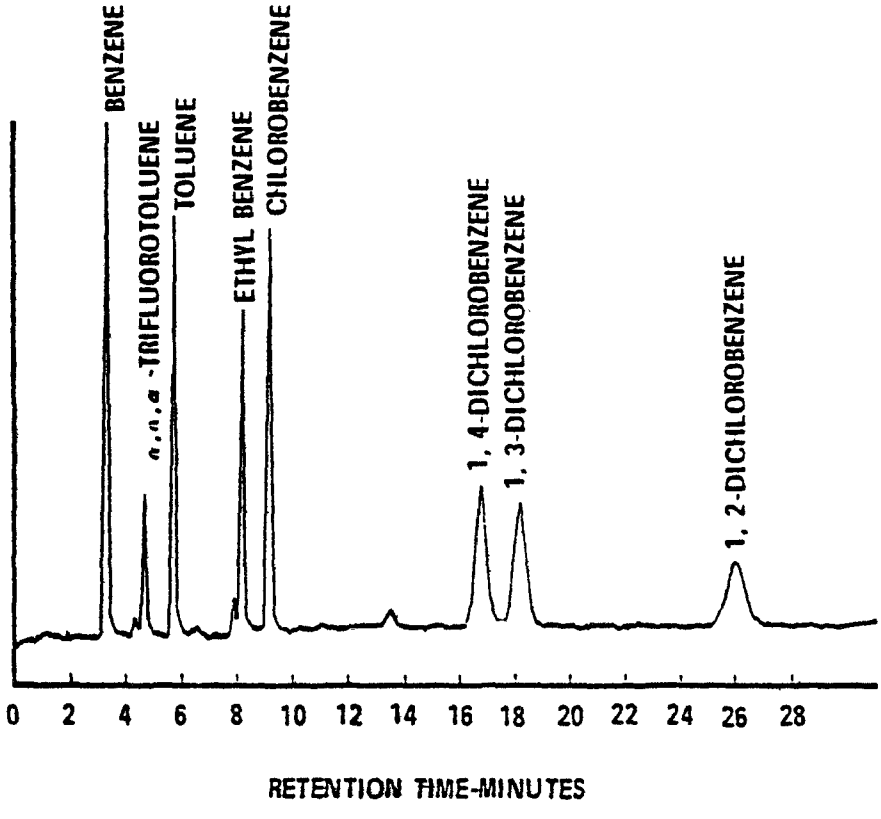


Figure 8.02-1
GAS CHROMATOGRAM OF VOLATILE AROMATICS

does not contain the specific contaminant, the analyst must demonstrate, using spiked samples, that the method sensitivity is $\leq$ 1 ug/gm of sample.

2. When duplicate and spiked samples are analyzed, all data obtained should be reported.

3. If one desires to determine the actual concentration of the compound in the waste, the method of standard addition should be used.

Table 8.02-1

CHROMATOGRAPHY

Compound	Retention Time (min)*	Detector Methods
Benzene	3.33	PID
Chlorobenzene	9.17	PID
1,4 Dichlorobenzene	16.8	PID
1,3 Dichlorobenzene	18.2	PID
1,2 Dichlorobenzene	25.9	PID
Ethyl ether		FID
Methyl ethyl ketone		FID
Methyl isobutyl ketone		FID
Toluene	5.75	PID
Xylene		PID

* 6' x 0.085 in. column packed with 1.75% Bentone 34 and 5% SP-2100 on Supelcoport 100/200.

Method 8.03

METHOD FOR ACRYLONITRILE, ACETONITRILE AND ACROLEIN

Scope and Application

This method is applicable to the determination of acrylonitrile, acetonitrile and acrolein in waste samples.

Summary of Method

The compounds are introduced into the gas chromatograph by either direct injection (Method 8.80), the headspace technique (Method 8.82) or the purge and trap technique (Method 8.83).

A temperature program is used in the gas chromatograph to separate the organic compounds for detection by a flame ionization detector (FID).

Interference

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum into the sample during shipment and storage. A sample blank carried through sampling and subsequent storage and handling protocols can serve as a check on such contamination.

Apparatus

1. Vial, 40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105°C before use.
2. Septum, teflon faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and

distilled deionized water, and dry at 105°C for one hour before use.

3. Sample introduction apparatus (see Methods 8.80, 8.82 or 8.83).
4. Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories, column supplies, recorder and gasses.

   A data system for measuring peak areas is recommended.
5. Chromosorb 101 80/100 mesh packed in a 6' x 1/8" O.D. stainless steel or glass column.
6. Syringes, 5 ml glass hypodermic with Luerlock tip (2 each).
7. Micro syringe, 10, 25, 100 ul.
8. 2-way syringe valve with Luer ends (3 each).
9. Syringe - 5 ml gas tight - with shut-off valve.
10. Vial, 15 ml screwcap, with teflon cap liner.

Reagents

1. Activated carbon, Filtrosorb - 200 (Calspan Corp.) or eqivalent.
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 distilled deionized water for about 15 minutes. Subsequently, while maintaining the temperature at 90°C,

bubble a contaminant-free inert gas through the water for one hour.

3. Stock standards - prepare stock standard solutions in propanol using assayed liquids or gas cylinder 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.
   a. Place about 9.8 ml of propanol into a 10 ml ground glass stoppered volumetric flask. Allow about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.
   b. Using a 100 ul syringe, immediately add all 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the propanol without contacting the neck of the flask.
   c. Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a teflon cap liner.
   d. Calculate the concentration in micrograms/liter from the net gain in weight.
   e. Store stock standards at 4°C. All standards must be replaced with fresh standard each month.

Calibration

1. Using stock standards, prepare secondary dilution standards in propanol that contain the compounds of interest, either singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in the Procedure section. By injecting secondary standards, adjust the sensitivity limit and the linear range of the analytical system for each compound being analyzed for a sensitivity of $\leq$ 1 ug (2 x background).

Quality Control

1. Before processing any samples, the analyst should demonstrate through the analysis of an organic-free water or solvent blank that the entire analytical system is interference free.
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 accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques should be used.
3. The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of this method in dealing with each sample matrix by

spiking each sample with known amounts of the compounds the waste is being analyzed for. Using these spiked samples, readjust the sensitivity of the instrument such that 1 ug/gm of sample can be readily detected.

Procedure

1. Assemble gas chromatograph with column specified in Apparatus section.
2. Set helium carrier gas at 45 ml/minute flow rate.
3. Hold column temperature at 80°C for 5 minutes, then program an 8°C/minute rise to 150°C and hold until all species have eluted.
4. Calibrate the system immediately prior to conducting any analyses and recheck as in Quality Control for each type of waste. Calibration should be done no less frequently than at the beginning and end of each analysis session. See Figure 8.03-1 for an example of the chromatogram to be expected using these conditions.

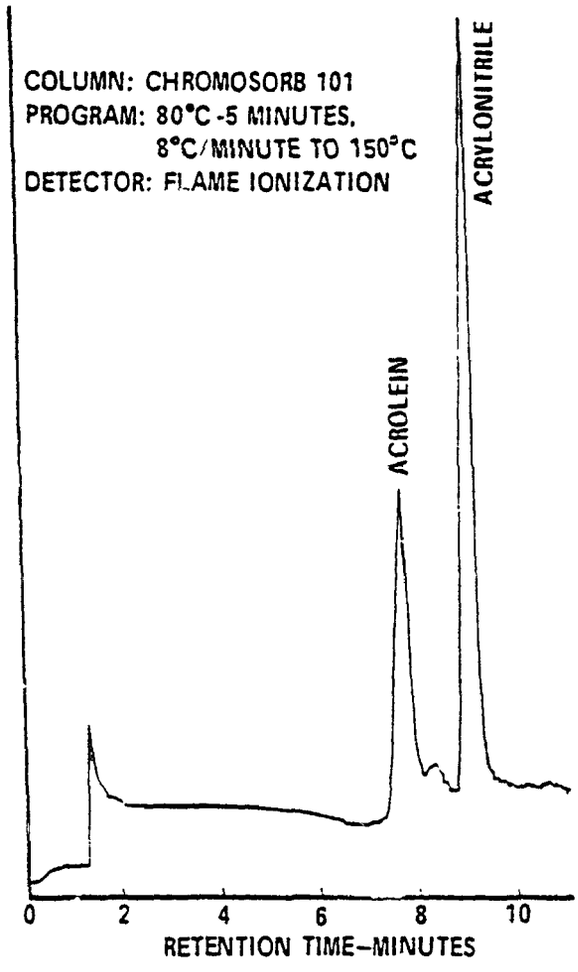


Figure 8.03-1
GAS CHROMATOGRAM OF ACROLEIN AND ACRYLONITRILE

Method 8.04

PHENOLS

Scope and Application

The following compounds may be determined by this method:

2-Chlorophenol

Cresol(s)

Cresylic acid(s)

2,4,-Dimethylphenol

4,6-Dinitro-o-cresol

4-Nitrophenol

Pentachlorophenol

Tetrachlorophenol

Trichlorophenol(s)

Summary of Method

The sample or sample extract is injected onto the gas chromatograph column following appropriate sample preparation procedures: (Shake out (Method 8.84), Soxhlet extraction (Method 8.86), or Sonication (Method 8.85)). A general clean-up procedure employing liquid-liquid extraction is described in Method 9.1. An optional clean-up procedure specific for this group of compounds is described at the end of this method, for samples or extracts which may require further clean-up. A temperature program is used in the GC system to separate the compounds before detection with a Flame Ionization Detector (FID) or Halogen Specific Detector (HSD).

The method also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives for electron capture gas chromatography with additional clean-up procedures to aid the analyst in the elimination of interferences.

Interferences

1. Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.
2. Interferences coextracted from samples will vary considerably from source to source depending upon the waste being sampled. While general cleanup techniques are provided in Section 9 and as part of this method, unique samples may require additional cleanup.

Apparatus

1. Vial with cap - 40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105°C before use.
2. Septum, teflon faced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled deionized water, and dry at 105°C for one hour before.
3. Sample introduction apparatus (Methods 8.80 or 8.82 or 8.83).

4. Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories, including FID or HSD, column supplies, recorder and gases. A data system for measuring peak area is recommended.
5. Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 1.8 meter long 2 mm ID glass column (Column 1) or Chromosorb W-AWDMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8 meter long X mm ID glass column (Column 2).
6. Syringes - 5 ml glass hypodermic with Luerlok tip (2each).
7. Micro syringe - 10, 25, 100 ul.
8. 2-way syringe valve with Luer ends (3 each).
9. Syringe - 5 ml gas tight with shut-off valve.
10. Bottle - 15 ml screw-cap, with teflon cap liner.
11. Kuderna-Danish apparatus (K-D) [Kontes K-570000 or equivalent] with 3 ball Snyder column.
12. Water bath - heated with concentric ring cover capable of temperature control (± 2°C). The bath should be used in a hood.
13. Chromatographic column - 10mm ID by 100mm length with teflon stopcock.
14. Reaction vial - 20 ml with teflon - lined cap.

Reagents

1. 2 - propanol - pesticide quality or equivalent
2. Stock standards - prepare stock standard solutions at a concentration of 1.0 ug/ul by dissolving 0.100 grams

of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 ml ground glass stopped 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.

3. PFB derivative reagents:
   a. Hexane and toluene - pesticide quality or equivalent
   b. Sodium sulfate - (ACS) granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).
   c. Potassium carbonate - (ACS) powdered.
   d. Silica gel - (ACS) 100/200 mesh, grade 923; activated at 130°C and stored in a dessicator.
   e. Pentafluorobenzyl bromide - 97% minimum purity.
   f. 1,4,7,10,13,16-Hexaoxacylooctadecane (18 crown 6) - 98% minimum purity.

Calibration

1. Using stock standards, prepare secondary dilution standards in 2-propanol that contain the compounds of interest, either singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those in the "procedure section." By injecting secondary standards adjust the sensitivity limit and the linear range of the analytical system for each compound being analyzed for to a sensitivity of $\leq$ 1 ug (2X background).

Quality Control

1. Before processing any samples the analyst should demonstrate through the analysis of an organic - free water or solvent blank that the entire analytical system is interference free.
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 accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram confirmatory techniques such as mass spectroscopy should be used.
3. The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of this method in dealing with each sample matrix by spiking each sample with known amounts of the compounds the waste is being analyzed for and using these spiked samples readjust the sensitivity of the instrument such that 1 ug/gm of sample can be readily detected (see Quality Control).

Flame Ionization Gas Chromatography Procedure

1. Assemble gas chromatograph with column 1 and Flame Ionization Detector (apparatus section).
2. Set nitrogen carrier gas at 30 ml/min flow rate.
3. Set column temperature at 80°C at injection and program to immediately rise at 8°C/min to 150°C.

Derivatization and Electron Capture Gas Chromatography Procedure

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.
2. Add about 3 mg of potassium carbonate to the solution and shake gently.
3. Cap the mixture and heat for 4 hours at 80°C in a hot water bath.
4. Remove the solution from the hot water bath and allow it to cool.
5. Add 10 ml hexane to the reaction vial and shake vigorously for one minute. Add 3.0 ml of distilled deionized water to the reaction vial and shake for two minutes.
6. Decant organic layer into a concentrator tube and cap with a glass stopper.
7. Pack a 10mm ID chromatographic column with 4.0 grams of activated silica gel. After settling the silica gel by tapping the column, add about two grams of anhydrous sodium sulfate to the top.
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 or standard. Elute the column with 10.0 ml of hexane (Fraction 1) and discard

this fraction. Elute the column, in order with 10.0 ml 15% toluene in hexane (Fraction 2), 10.0 ml 40% toluene in hexane (Fraction 3), 10.0 ml 75% toluene in hexane (Fraction 4), and 10.0 ml 15% 2-propanol in toluene (Fraction 5). Elution patterns for the phenolic derivatives are shown in Table 8.04-2 Fractions may be combined as desired depending upon the specific phenols of interest or level of interferences. Collect the fractions in appropriate sized K-D apparatus and concentrate each fraction to 10 ml.

9. Assemble gas chromatograph with column 2 and HSD (apparatus section).
10. Using 5% methane/95% argon as the carrier gas adjust flow to 30 ml/min.
11. Set column temperature at 200°C.
12. Inject 2-5ml of the appropriate fraction using the solvent - flush technique. Smaller (1.0 ml) volumes can be injected if automatic devices are employed. Record volume injected to the nearest 0.05 ml and the resulting peak size in area units. If the peak area exceeds the linear range of the system dilute the extract and reanalyze.

Calibrate the system immediately prior to conducting any analyses and recheck as in Quality Control for each type of waste. Calibration should be done no less frequently than at the beginning and end of each session.

Calculations

1. If a response for the contaminant being analyzed for is greater than 2X background is noted, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm.
2. When duplicate and spiked samples are analyzed, all data obtained should be reported.
3. If one desires to determine the actual concentration of the compound in the waste, the method of standard addition should be used.

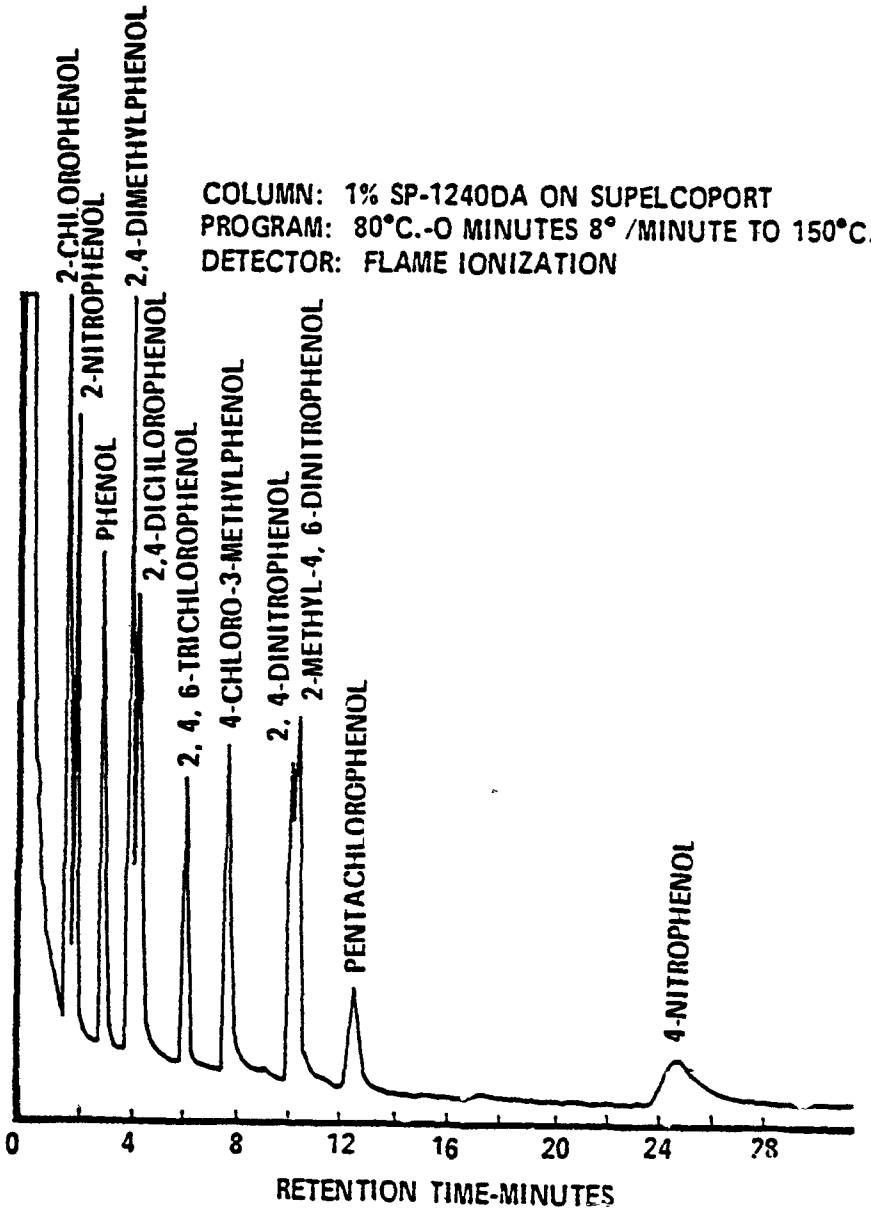


Figure 8.04-1
GAS CHROMATOGRAM OF PHENOLS

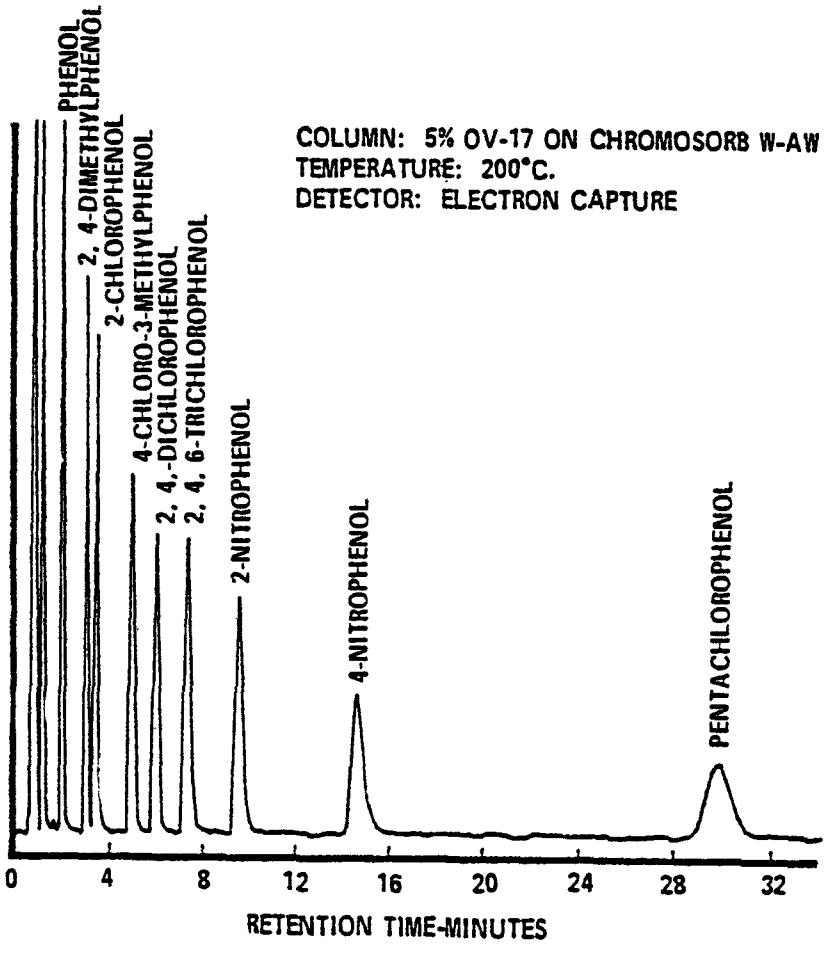


Figure 8.04-2
GAS CHROMATOGRAM OF PFB DERIVATIVES OF PHENOLS

Table 8.04-1

FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compounds	Retention Time* (minutes)
2-Chlorophenol	1.70
Cresol(s)	
Cresylic acid	
2,4-Dimethylphenol	4.03
4,6-Dinitro-O-cresol	
4-Nitrophenol	24.25
Pentachlorophenol	12.42
Phenol	3.01
Tetrachlorophenol	
2,4,6-Trichlorophenol	6.05

*Column 1

Table 8.04-2

ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES

Parent compound	Retention time (minutes)*	Recovery percent by fraction				
		1	2	3	4	5
2-Chlorophenol	3.3			90	>1	
Phenol	1.8			90	10	
2,4-Dimethyphenol	2.9			95	7	
2,4,6-Trichlorophenol	7.0		50	50		
Pentachlorophenol	28.8		75	20		
4-Nitrophenol	14.0				>1	90

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.

*Column 2

Method 8.06

GAS CHROMATOGRAPHY GENERAL METHOD FOR EXTRACTABLE ORGANICS

Scope and Application

This is a general gas chromatographic method suitable for the determination of the presence of the following compounds in RCRA materials:

Formic acid

Heptachlor

Hexachlorethane

Hexachloracyclopentadiene

Maleic anhydride

Naphthoquinone

Phosphorodithioic acid esters

Phthalic anhydride

2-Picoline

Pyridine

Toluene Diisocyanate(s)

Prior to using this method waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method (e.g., shake out, soxhlet extraction, sonication).

Summary of Method

Chromatographic conditions are described which allow for the measurement of the presence of the compounds in the extract at levels sufficient to determine the presence of the compounds in the original waste at a concentration of 1 ug/gram.

If interferences are encountered during chromatography the method provides a general purpose cleanup procedure to aid the analyst.

Precaution

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baseline causing misinterpretation of gas chromatograms. All of these materials should be demonstrated to be free from interferences under the conditions of the analysis by running method blanks in order to prevent difficulties during the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required to eliminate interferences.

Interfering substances coextracted from the sample will vary considerably from source to source, depending upon the diversity of the waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities required.

Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst should demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis before deciding that the compound being analyzed for is actually present. Of particular importance is the avoidance of plactics such as polyvinyl chloride because phthalates are commonly used as plasticizers and are easily extracted.

Apparatus

1. Vial with cap - 40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105°C before use.
2. Septum - teflon - forced silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and distilled dionized water, and dry at 105°C for one hour before.
   Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories, including Halogen Specific or Flame Ionization Detector, column supplies, recorder and gases. A data system for measuring peak area is recommended.
3. Supelcoport 100/120 mesh, coated with 1.5% SP-2250 + 1.95% SP-2401 in a 180 cm long x 4 mm ID glass column (column 1) or Supelcoport, 100/120 mesh, coated with 3% OV-1 in a 180 cm long x 4 mm ID glass column (column 2).
4. Syringes - 5 ml glass hypodermic with luerlok tip (2 each).
5. Micro syringe - 10, 25, 100 ul.
6. 2-way syringe valve with Luer ends (3 each).
7. Syringe - 5 ml gas-tight with shut-off valve.
8. Bottle - 15 ml screw-cap, with teflon cap liner.
9. Drying column - 20 mm ID pyrex chromatograph column with coarse frit.
10. Kuderna-Danish (K-D) Apparatus equipped with the appropriate Synder columns [Kontes K-570000 or equivalent].
11. Boiling chips - solvent extracted, approximately 10/40 mesh.

12. Water Bath - heated, with concentrating cover, capable of temperature control (2°C). The bath should be used in a hood.
13. Chromatography column-300 mm long x 10 mm ID with coarse fritted disc at bottom and Teflon stopcock. (Kontes K-420540-0213 or equivalent).

Reagents

1. Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).
2. Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.100 grams of assayed reference material in pesticide quality iso-octane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.
3. Diethyl Ether - Nanograde, redistilled in glass if necessary. Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Boulevard, Elmsford, N.Y. 10523.) 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.

4. Florisil - PR grade (60/200 mesh); purchase activated at 1250°F and store in dark in glass container with ground glass stoppers or foil-lined screw caps.
5. Hexane - Pesticide Quality

Calibration

1. Prepare calibration standards that contain the compounds of interest either singly or mixed together.
2. Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in the Gas Chromatography section. By injecting calibration standards, adjust the sensitivity of the detector and the analytical system for each compound being analyzed for so as to detect $\leq$ 1 ug of the compound.
3. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to determine elution patterns and the absence of interferences from the reagents.

Quality Control

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.

2. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technque. 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 samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug of the compound per gm of sample then the sensitivity of the instrument should be increased or the sample should be subjected to additional clean up. 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 chromatogram, confirmatory techniques such as mass spectroscopy should be used.

Cleanup

1. If the entire extract is to be cleaned up to remove interferences it must first be concentrated to about 2 ml:

a. To the K-D apparatus, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml hexane through the top. Place the K-D apparatus on a hot water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the volume of

liquid reaches about 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Synyder column and rinse its lower joint into the concentration tube with 0.2 ml of hexane.

2. Florisil Column Clean-up

In order to employ the Florisil column cleanup procedure the analyst will have to determine using standards the elution pattern of each compound to be analyzed for. Once this has been done the following procedure can be followed to effect cleanup of the sample.

a. Place 100 g of Florisil into a 500 ml beaker and heat for approximately 16 hours at 400°C. After heating transfer to a 500 ml reagent bottle. Tightly seal and cool to room temperature. When cool add 3 ml of distilled water which is free of phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

b. Place 10g of this Florisil preparation into a 10 mm ID chromatography column and tap the column to settle the Florisil. Add 1 cm of anhydrous sodium sulfate to the top of the Florisil.

c. 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 sample onto the column using an additional 2 ml of hexane to complete the transfer.

d. Just prior to exposure of the sodium sulfate layer to the air add 40 ml hexane and continue the elution at the rate of 2 ml/minute. This eluate is Fraction 1. Concentrate the fraction by standard K-D technque. No solvent exchange is necessary. After concentration and cooling, transfer the 10 ml volumetric flask, dilute to 10 ml and analyze by gas chromatography.

e. Next elute the Florisil with 100 ml of 5 percent ethyl ether/95% hexane (v/v) and concentrate as in step d. [Fraction 2].

f. Next, elute with 100 ml of 15% ethyl ether/85% hexane (v/v) and concentrate Fraction 3 as in step d.

g. Elute with 100 ml of 50% ethyl ether/50% hexane (v/v), and concentrate, Fraction 4 as in step d.

h. Finally, elute with 100 ml of ethyl ether, and concentrate, Fraction 5 as in step d.

Gas Chromatography

1. Assemble gas chromatograph with either Column 1 or 2 (see Apparatus).

Column 1 (Supelcoport 100/120 with 1.5% SP 2250 + 1.95% SP 2401)

a. Set carrier gas at 60 ml/minute flow rate.

b. Column temperatures will vary from 180°C to 220°C depending on the compound.

Column 2 (Supelcoport 100/120 with 3% OV-1)

a. Set carrier gas at 60 ml/min flow rate.

b. Column temperature will vary from 200°C to 220°C depending on the compound.

2. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with calibration standards.
3. Inject 2-5 ul of the sample extract or appropriate Florisil eluate using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.
4. If a response for the contaminant being analyzed for is greater than 2x background, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the method sensitivity is $\leq$ 1 ug of compound per gm of sample.
5. If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

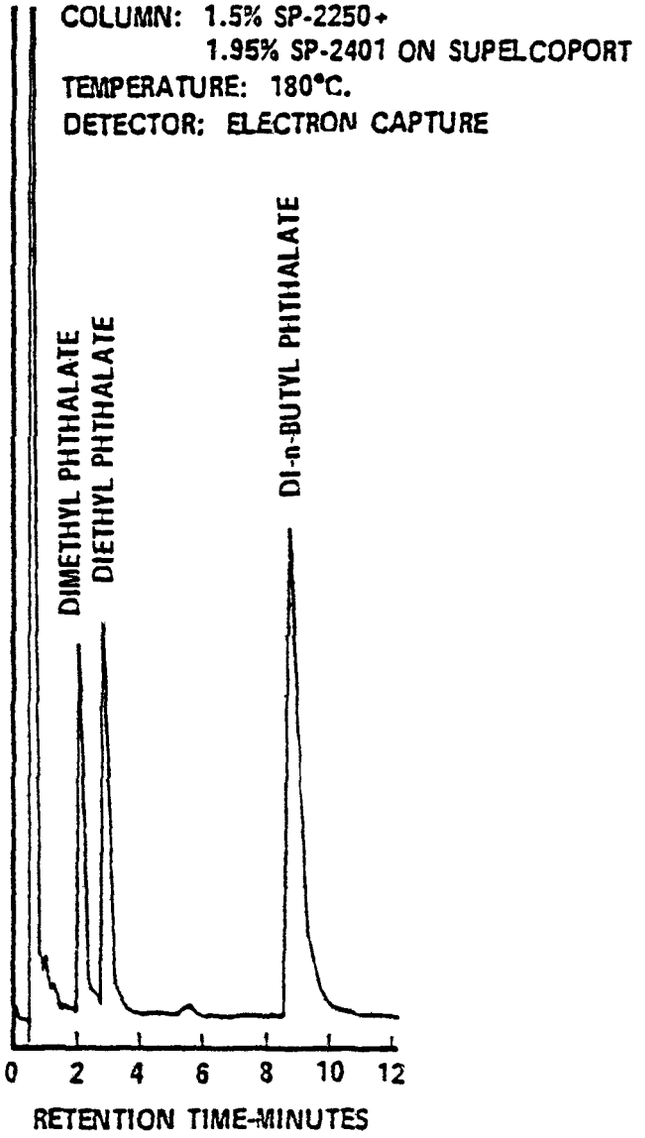


Figure 8.06-1
GAS CHROMATOGRAM OF PHTHALATES

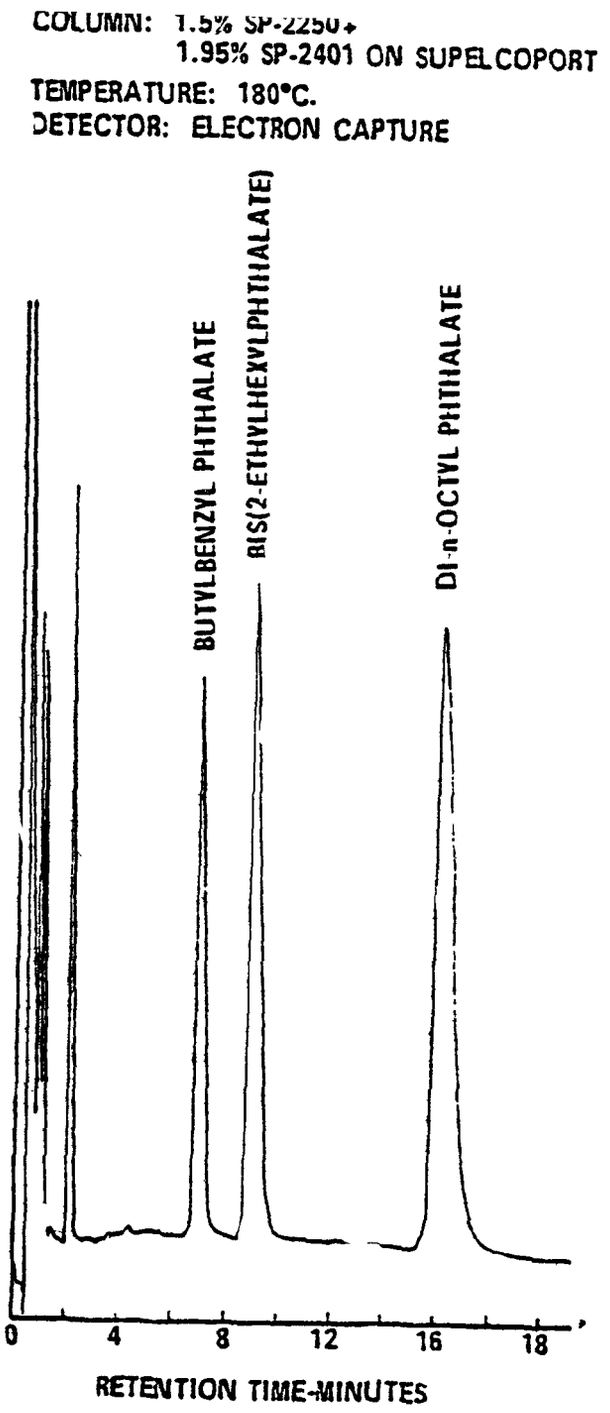


Figure 8.06-2
GAS CHROMATOGRAM OF PHTHALATES

Method 8.08

GC METHOD FOR ORGANOCHLORINE PESTICIDES AND PCB's

Scope and Application

This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCB's). The following compounds may be determined by this method:

Chlordane

Chlorinated biphenyls

Endrin

Heptachlor

Lindane

Methoxychlor

Toxaphene

Summary of Method

Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method (i.e. shake out, sonication, or soxhlet extraction). This method provides chromatographic conditions for the detection of $\geq$ 1 mg/l of the compounds in the extract.

If interferences are encountered, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these

materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the waste being sampled. While a general cleanup technique is provided as part of this method, unique samples may require additional cleanup.

Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with the use of a microcoulometric or electrolytic conductivity detector.

Apparatus

1. Kuderna-Danish (K-D) Apparatus, equipped with a 3 ball Snyder column (Kontes K-570000 or equivalent).
2. Boiling chips--extracted with extraction solvent, approximately 10/40 mesh.
3. Water bath, heated, with concentric ring cover, capable of temperature control ($^{+}2^{\circ}C$). The bath should be used in a hood.
4. Gas chromatograph--Analytical system complete with gas chromatograph suitable for on-column injection and all required acessories including electron capture or halogen specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.
5. Chromatographic column-Pyrex, 400 mm X 25 mm OD, with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

Reagents

1. Methylene chloride-Pesticide quality or equivalent.
2. Sodium Sulfate (ACS) Granular anhydrous (purified by heating at $400^{\circ}C$ for 4 hrs. in a shallow tray).
3. Stock standards--Prepare stock standard solutions at a concentration of 1.0 ug/ul by dissolving 0.100 grams of reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. Store the solution in a refrigerator. Check stock solutions frequently for signs

of degradation or evaporation, especially just prior to preparing working standards from them.

4. Mercury, triple distilled.
5. Hexane, pesticide residue analysis grade.
6. Isooctane (2,2,4-trimethyl pentane), pesticide residue analysis grade.
7. Acetone, pesticide residue analysis grade.
8. Diethyl ether, Nanograde, redistilled in glass if necessary. Must be free of peroxides as indcated by EM Quant Test Strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd, Elmsford, N.Y., 10523).
9. Florisil, PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil lined screw caps. Before use activate each batch at least 16 hours at 130°C in foil covered glass container.

Calibration

1. Prepare calibration standards that contain the compounds of interest, either singly or mixed together.
2. Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 8.08-1. By injecting calibration standards, adjust the sensitivity of the detector and of the analytical system for each compound being analyzed for so as to detect $\leq$ 1 ug.
3. The cleanup procedure utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested.

The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 grams.

4. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

Quality Control

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.
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 samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug/gm 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 chromatogram, confirmatory techniques such as mass spectroscopy should be used.

Cleanup and Separation

Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise disfigure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

Florisil Column Cleanup:

1. Add a weight of Florisil, (nominally 21g,) predetermined by calibration to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1-2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.
2. Adjust the sample extract volume to 10 ml and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 ml hexane, adding each rinse to the column.
3. Place a 500 ml K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column

with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K-D flask and set aside for later concentration.

4. 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 in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 8.08-2.
5. Concentrate the eluates by standard K-D techniques, 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.
6. Elemental sulfur will usually elute entirely in Fraction 1. To remove sulfur interference from this fraction or the original extract, pipet 1.00 ml of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1-3 drops of mercury and seal. Agitate the contents of the vial for 15-30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker for 2 hours. Analyze by gas chromatography.

Gas Chromatography

Table 8.08.1 summarizes some recommended gas chromatographic column materials, operating conditions for the instrument, and some estimated retention times. Examples of the separations achieved by these columns are shown in Figures 8.08-1 through 8.08-10. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with the

compound of interest in order to insure a sensitivity of $\leq$ 1 ug/gm of original waste tested.

1. Inject 2-5 ul of the sample extract using the solvent flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.
2. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze. If the peak area measurement is prevented by the presence of interferences, further cleanup is required.
3. If detectable amounts of the compounds of interest are detected the waste does not meet the criteria for delisting of being fundamentally different from that of the listed waste.

Bibliography

1. Mills, P.A., "*Variation of Florisil Activity: Simple* Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29(1968).

Table 8.08.1

GAS CHROMATOGRAPHY OF PESTICIDES AND PCB's

Compound	Retention zone (min) Col. 1[1]	Col. 2[2]
Chlordane	(3)	(3)
Endrin	6.55	8.10
Lindane		
Toxaphene	(3)	(3)
PCB-1016	(3)	(3)
PCB-1221	(3)	(3)
PCB-1232	(3)	(3)
PCB-1242	(3)	(3)
PCB-1248	(3)	(3)
PCB-1254	(3)	(3)
PCB-1260	(3)	(3)

1. Supelcoport 100/120 mesh, coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/minute flow rate. Column temperature is 200°C.

2. Supelcoport 100/120 mesh, coated with 3% OV-1 in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/minute flow rate. Column temperature is 200°C.

3. Multiple peak response. See Figures 8.08-2 through 8.08-10.

Table 8.08.2

DISTRIBUTION AND RECOVERY OF CHLORINATED PESTICIDES AND PCBs USING FLORISIL COLUMN CHROMATOGRAPHY

Compound	Recovery (percent) by fraction		
	6% ethyl ether	15% ethyl ether	50% ethyl ether
Chlordane	100		
Endrin	4	96	
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

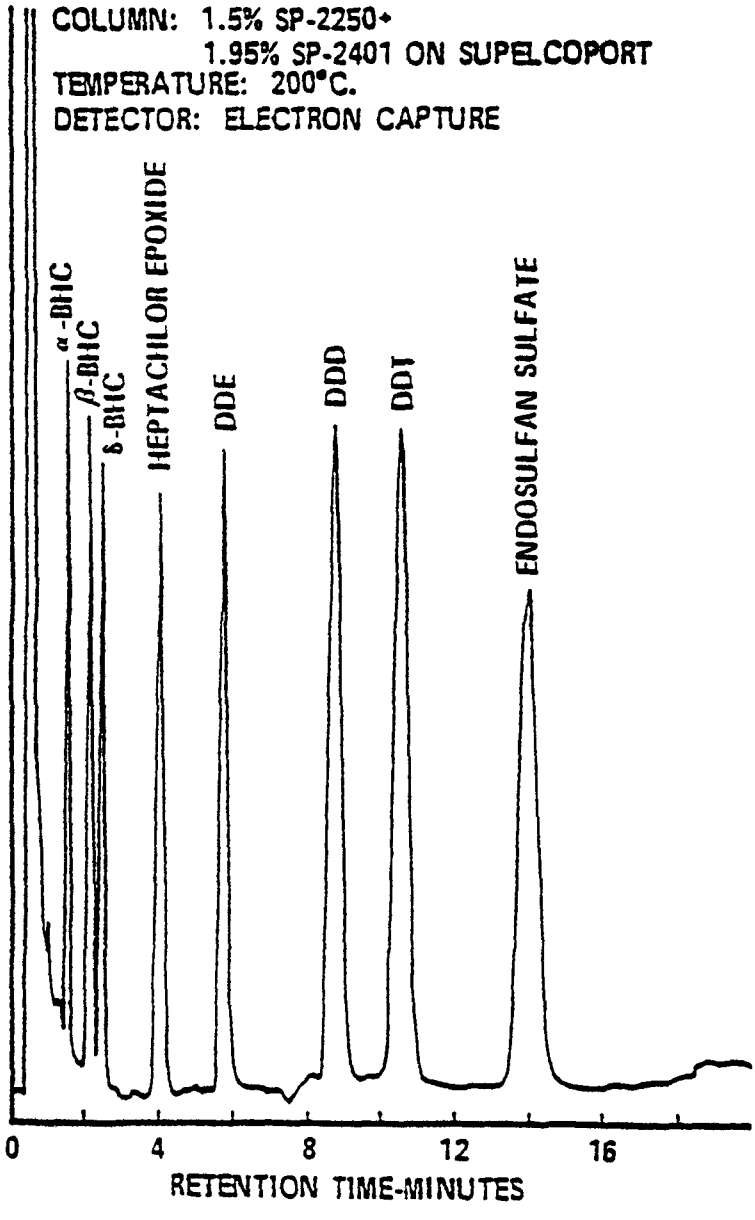


Figure 8.08-1
GAS CHROMATOGRAM OF PESTICIDES

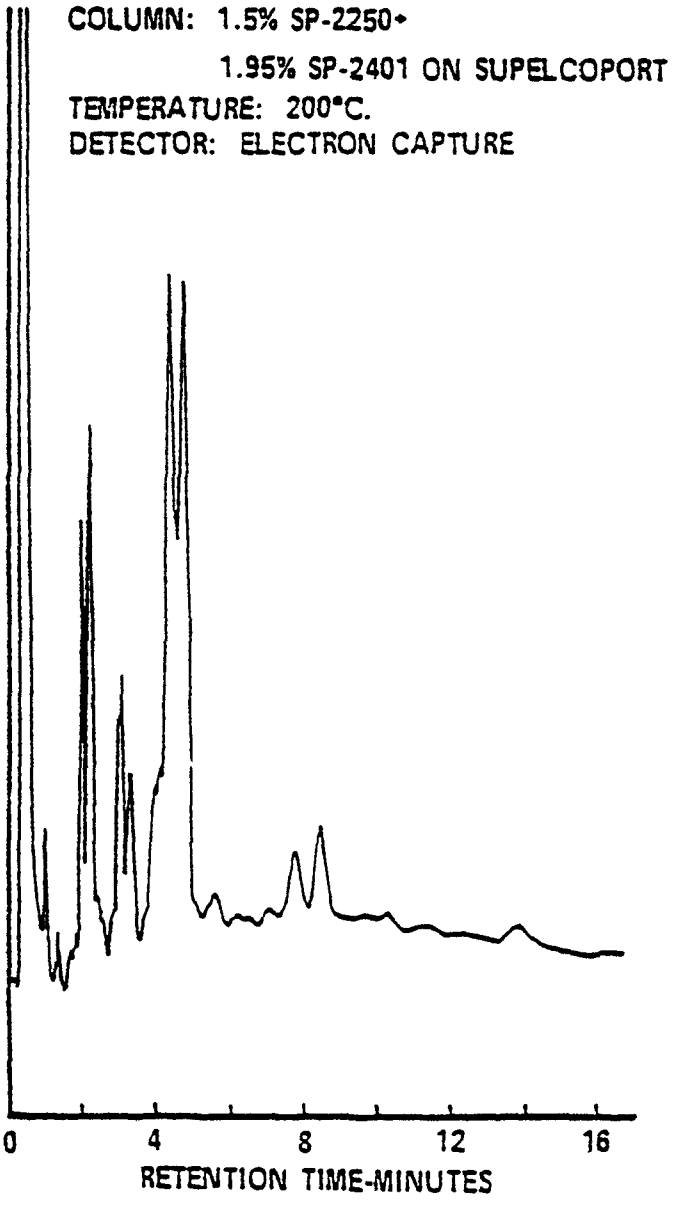


Figure 8.08-2
GAS CHROMATOGRAM OF CHLORDANE

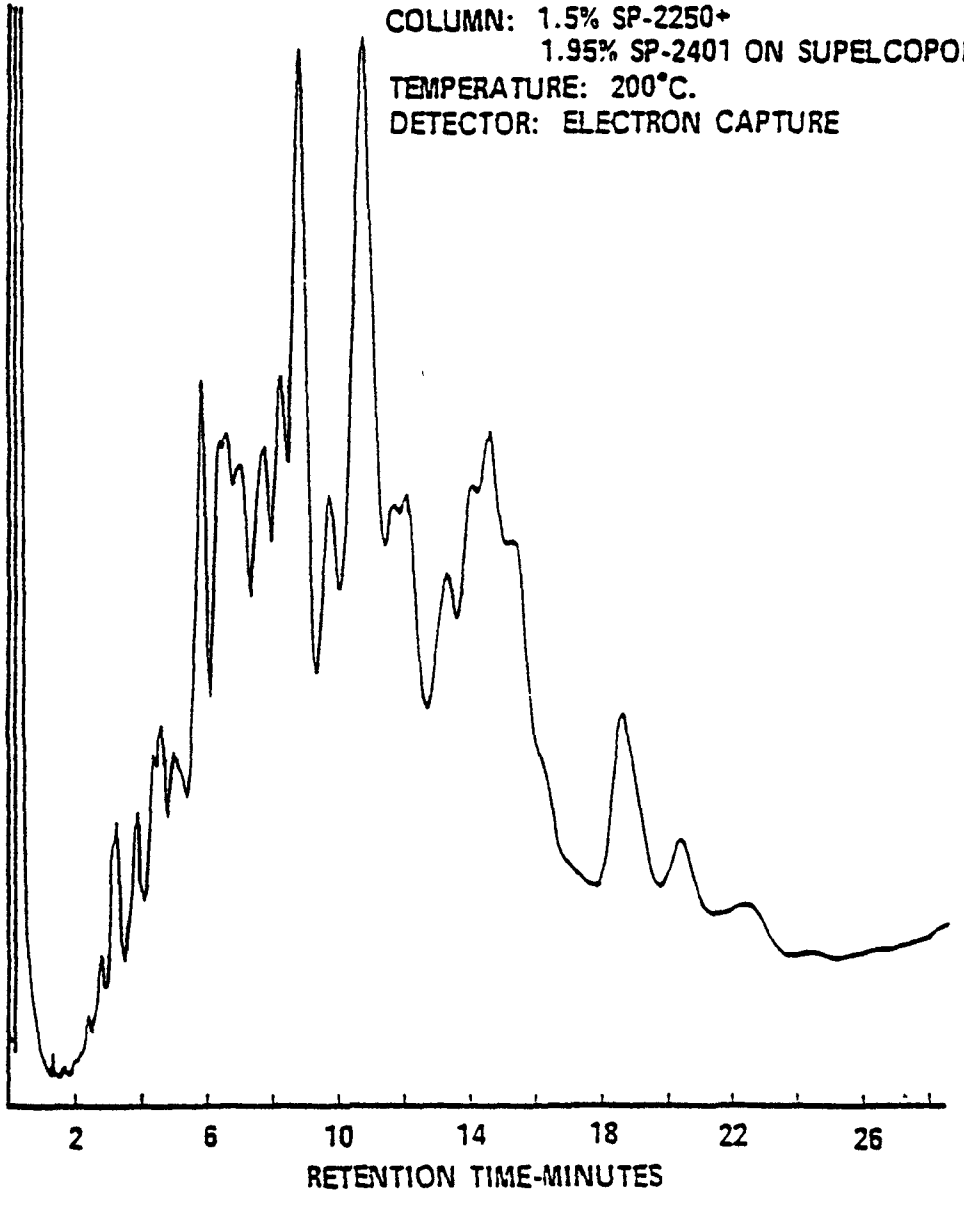


Figure 8.08-3
GAS CHROMATOGRAM OF TOXAPHENE

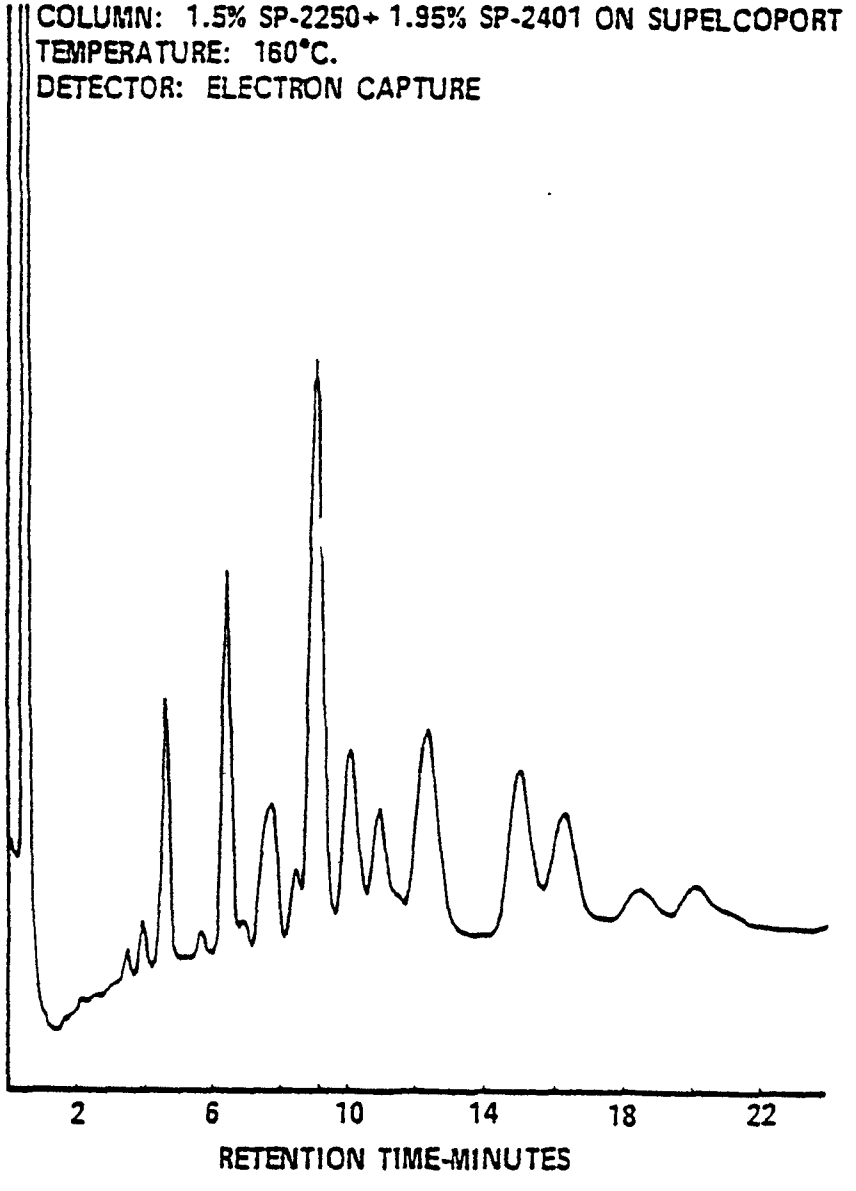


Figure 8.08-4
GAS CHROMATOGRAM OF PCB-1016

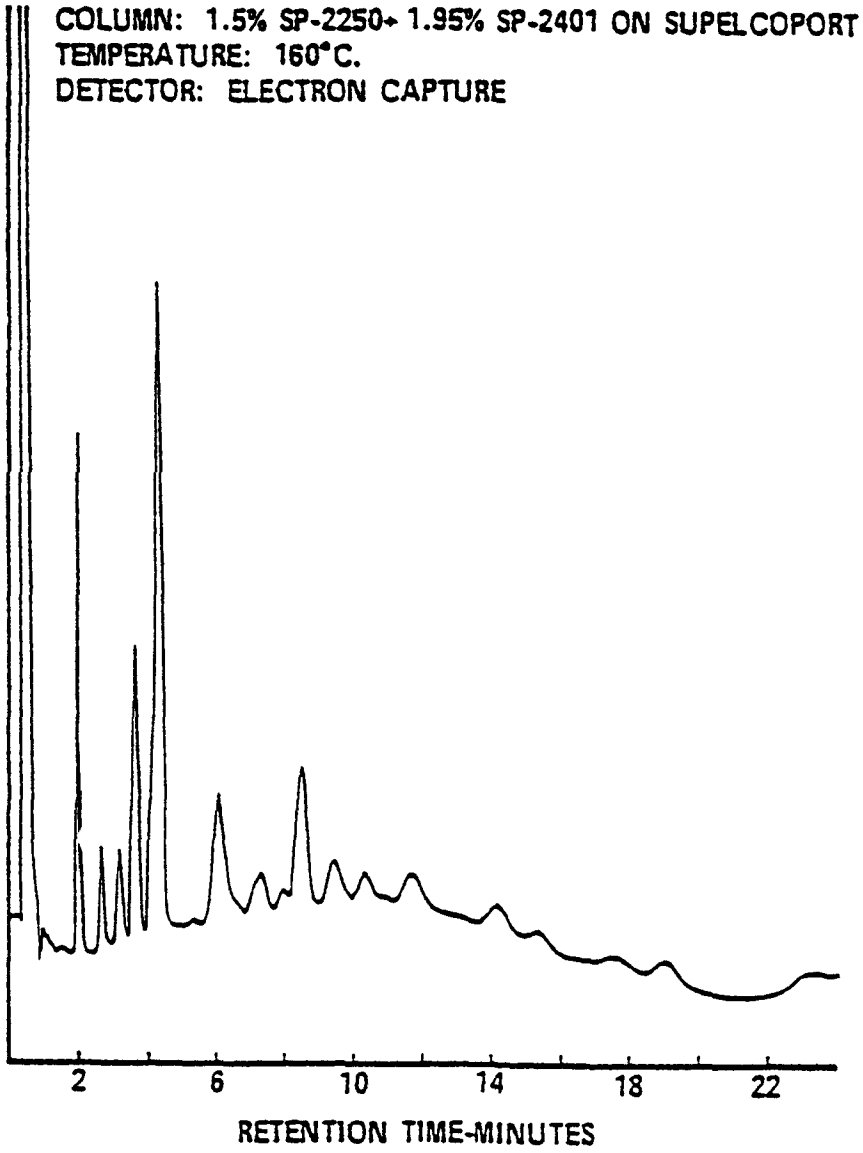


Figure 8.08-5
GAS CHROMATOGRAM OF PCB-1221

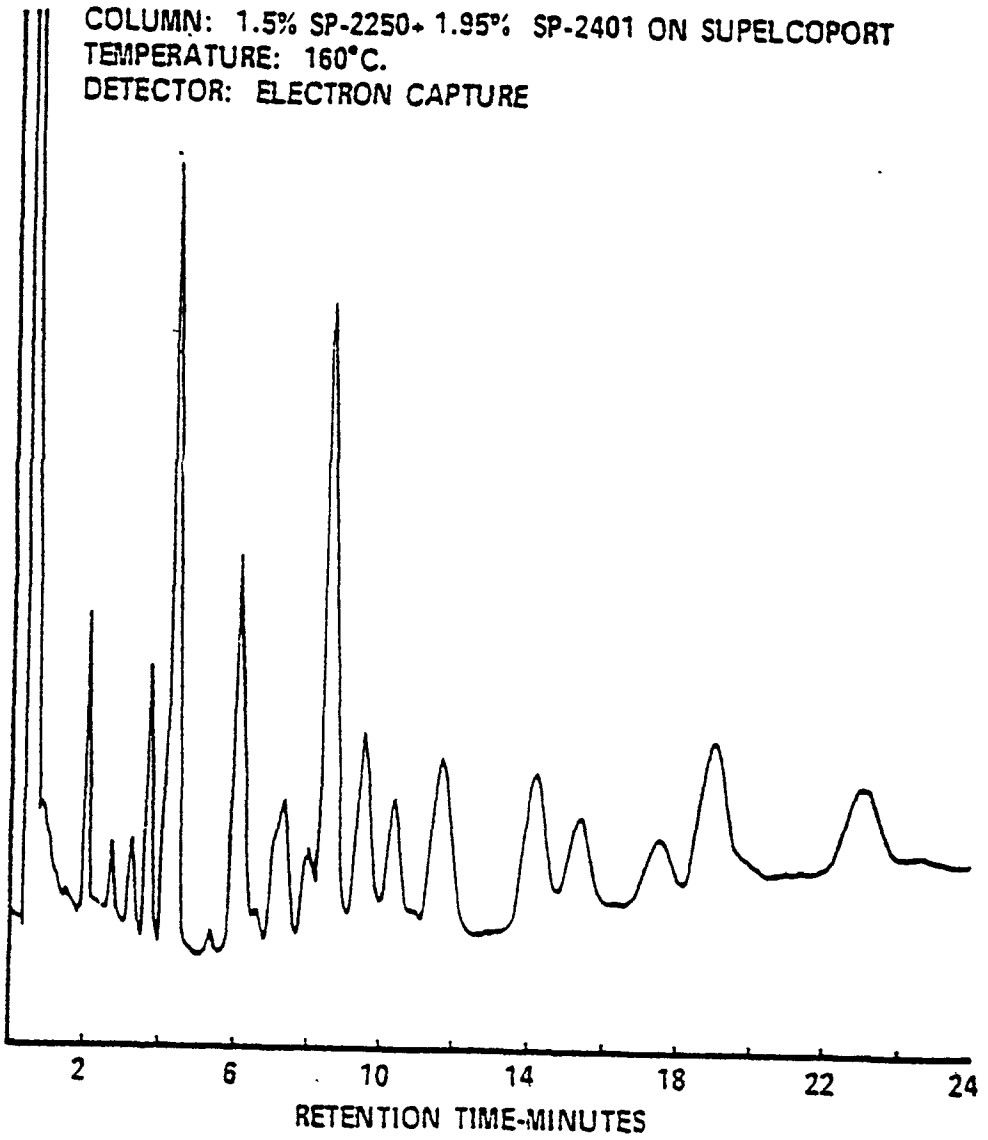


Figure 8.08-6
GAS CHROMATOGRAM OF PCB-1232

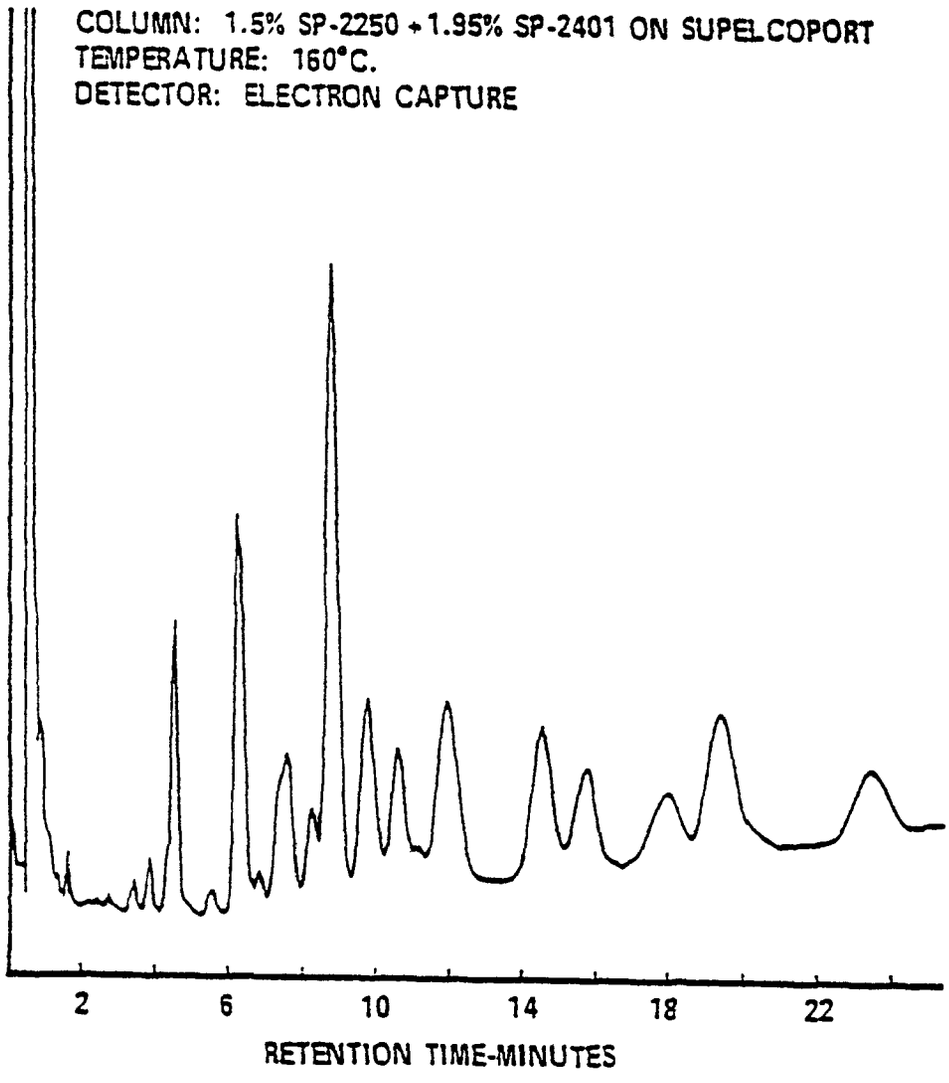


Figure 8.08-7
GAS CHROMATOGRAM OF PCB-1242

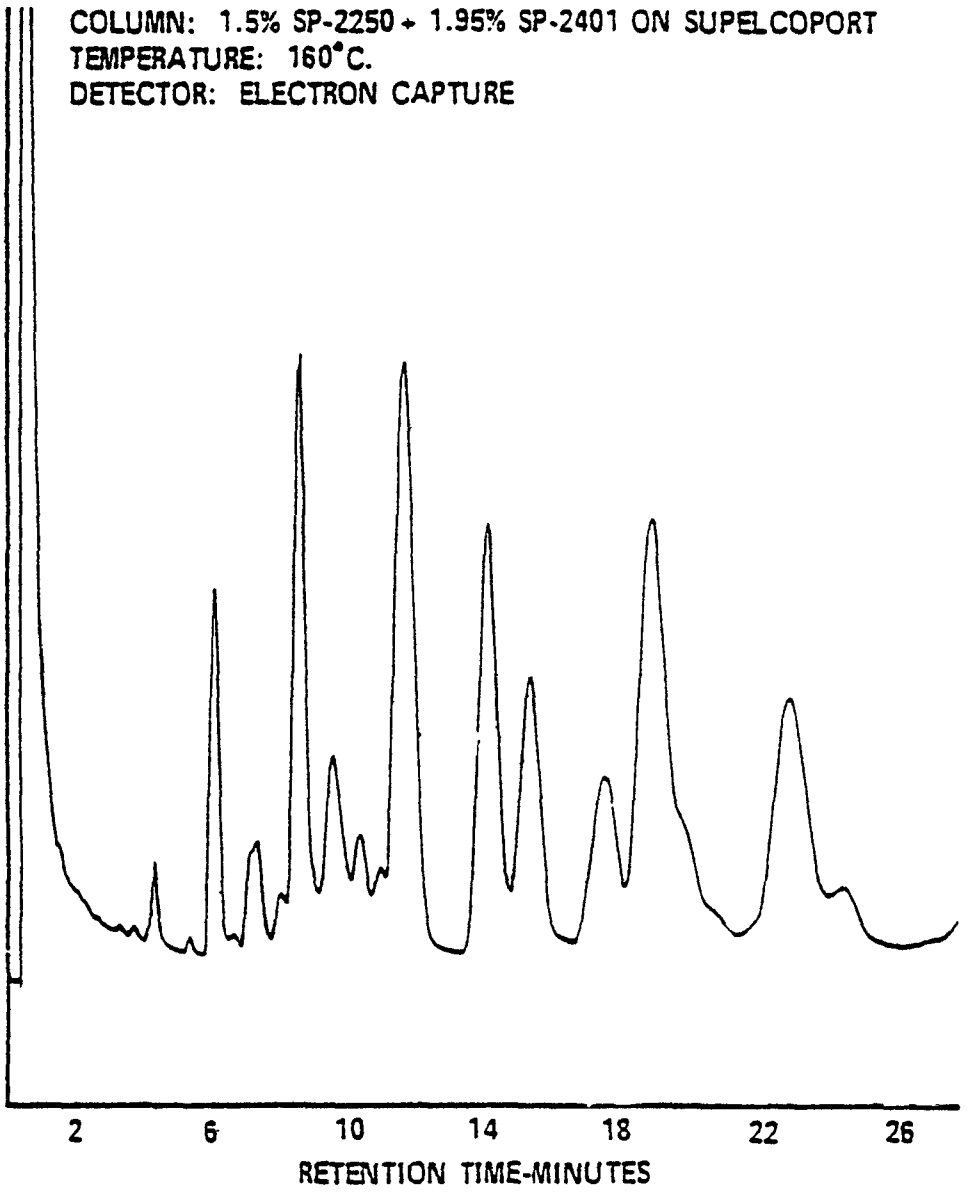


Figure 8.08-8
GAS CHROMATOGRAM OF PCB-1248

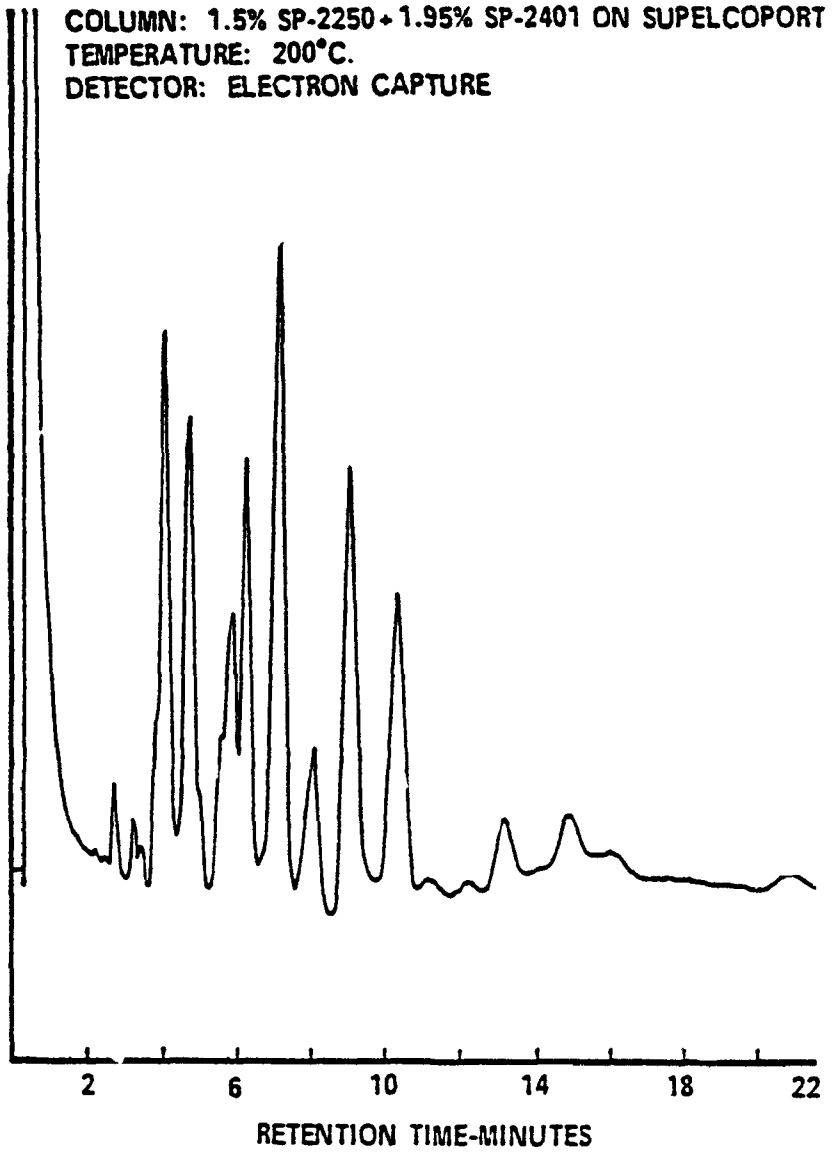


Figure 8.08-9
GAS CHROMATOGRAM OF PCB-1254

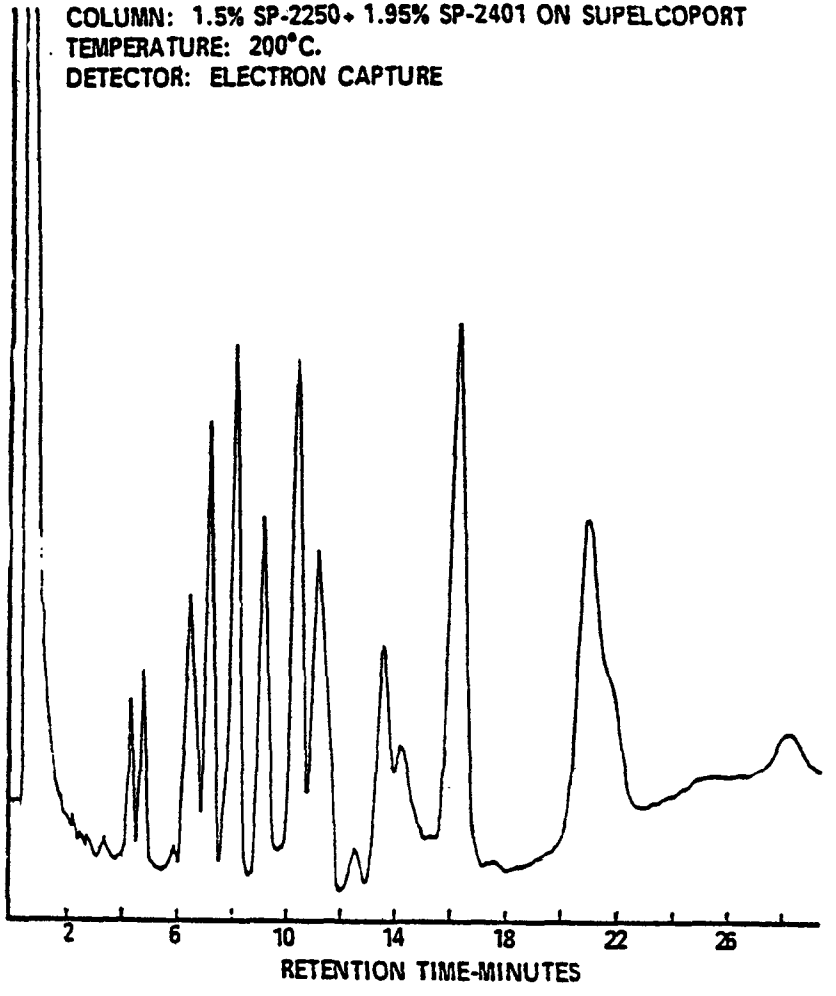


Figure 8.08-10
GAS CHROMATOGRAM OF PCB-1260

Method 8.09

GC METHOD FOR SEMIVOLATILE AROMATICS AND PHOSPHORODITHIOIC ACID ESTERS

Scope and Application

This method covers the determination of the following compounds:

Compounds	Detector
Dinitrobenzene	FID
2,4-Dinitrotoluene	ECD
Naphthoquinone	FID
Nitrobenzene	FID
Phosphorodithioic acid esters	FID
Phthalic anhydride	FID
2-Picoline	FID
Pyridine	FID

Prior to using this method, the waste samples should be prepared for chromatography,if necessary, using the appropriate sample preparation method (i.e. shake out, sonication, or soxhlet extraction). This method provides gas chromatographic techniques for measurement of the compound(s) of interest. Flame ionization or electron capture detection may be used, depending on the compound(s) of interest.

Summary of Method

If interferences are encountered the method provides a general purpose cleanup procedure to aid the analyst in their elimination.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the waste being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup.

Apparatus

1. Kuderna-Danish (K-D) Apparatus including:
   a. Concentrator tube-10ml. 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.
   b. Evaporative flask-500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K503000-0121 or equivalent).
   c. Snyder column-three-ball macro (Kontes K503000-0121 or equivalent).
   d. Snyder column-two ball micro (Kontes K-569001-0219 or equivalent).

2. Boiling chips - solvent extracted, approximately 10/40 mesh.
3. Water bath - heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.
4. Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including both electron capture and flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.
5. Chromatography column - 400 mm long x 10 mm ID, with coarse fritted plate on bottom and Teflon stopcock.

Reagents

1. Methylene chloride - Pesticide quality or equivalent.
2. Sodium sulfate - (ACS) Granular anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).
3. Stock standards - prepare stock standard solutions at a concentration of 1.0 ug/ul by dissolving 0.100 grams of 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.

4. Acetone, hexane, methanol, toluene - pesticide quality or equivalent.
5. Florisil-PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil lined screw caps. Before use, activate each batch overnight at 200°C in glass containers loosely covered with foil.

Calibration

Prepare calibration standards that contain the compounds of interest, either singly or mixed together.

Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 8.09-1. By injecting calibration standards adjust sensitivity of the detector and the analytical system for each compound being analyzed for so as to detect $\leq$ 1 ug.

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.

Quality Control

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.

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 precision and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug/gram of sample, the sensitivity of the instrument should be increased or the sample subjected to additional clean up. 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 chromatogram, confirmatory techniques such as mass spectroscopy should be used.

Cleanup and Separation

1. Prepare a slurry of 10g of activated Florisil in 10% methylene chloride in hexane (V/V). Use it to pack a 10 mm chromatography column gently tapping the column to settle the Florisil. Add 1 cm anhydrous sodium sulfate to the top of the Florisil.
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.

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. Elution should be at a rate of about 2 ml per minute. Discard the eluate from this fraction.
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. Concentrate the collected fraction by the K-D technique described in Method 9.01 including the solvent exchange into 1 ml toluene. This fraction should contain the compounds of interest.
5. Analyze by gas chromatography.

Gas Chromatography

1. Dinitrotoluene is analyzed by a separate injection into an electron capture gas chromatograph. The other compounds covered by this method are analyzed by injection of a portion of the extract into a gas chromatograph with a flame ionization detector. Table 8.09-1 summarizes some recommended chromatographic column materials and operating conditions for the instruments. Included in this table are estimated retention times. Examples of the separations achieved by the primary column are shown in Figures 8.09-1 and 8.09-2. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with each of the compounds of interest.
2. Inject 2-5 ul of the sample extract using the solvent flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed.

3. If a response for the contaminant being analyzed is greater than 2X background, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using spiked samples, that the instrument sensitivity is $\leq$1 ug/gm of sample.

Table 8.09-1

GAS CHROMATOGRAPHY RETENTION TIMES

Compound	Retention time (min)	
	Column A	Column B
Nitrobenzene	3.31	4.31
2,4-Dinitrotoluene	5.35	6.54
2,6-Dinitrotoluene	3.52	4.75

A. Gas-Chrom Q, 80/100 mesh, coated with 1.95% OF-1/1.5% OV-17 packed in a 4' x 1/4" OD. 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.

B. Gas-Chrom Q, 80/100 mesh, coated with 3% OV-101 packed in a 10' x 1/4" OD 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.

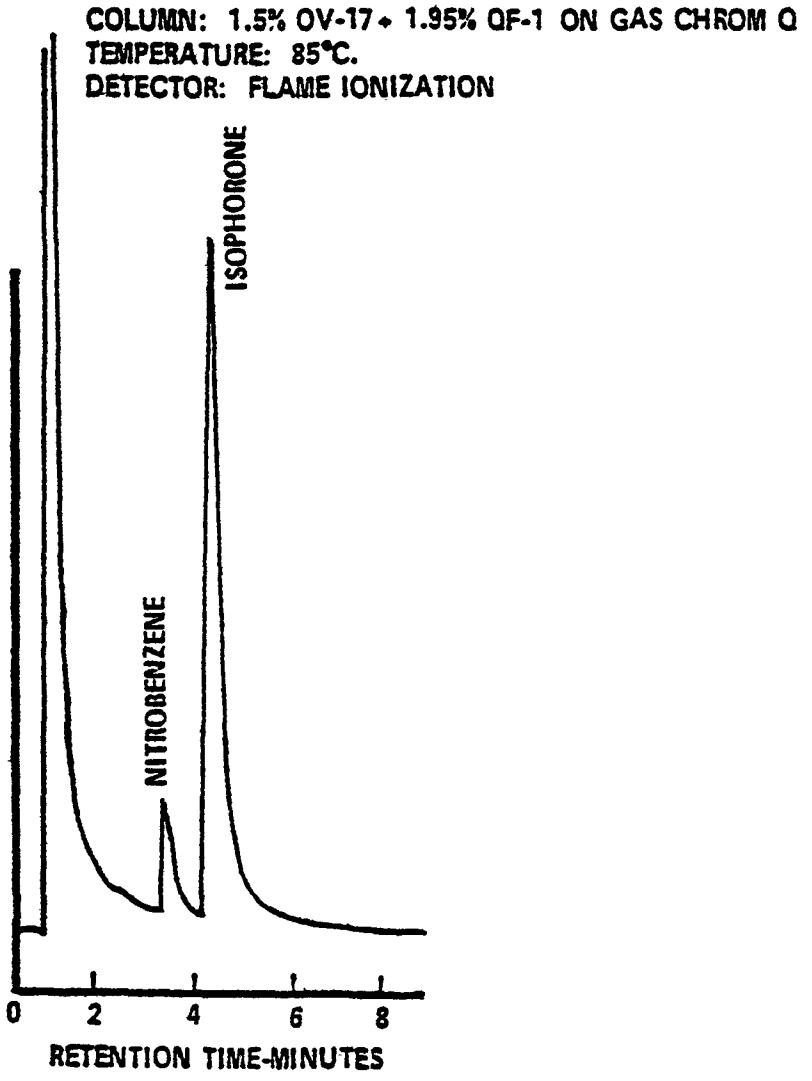


Figure 8.09-1
GAS CHROMATOGRAM OF NITROBENZENE AND ISOPROPANE

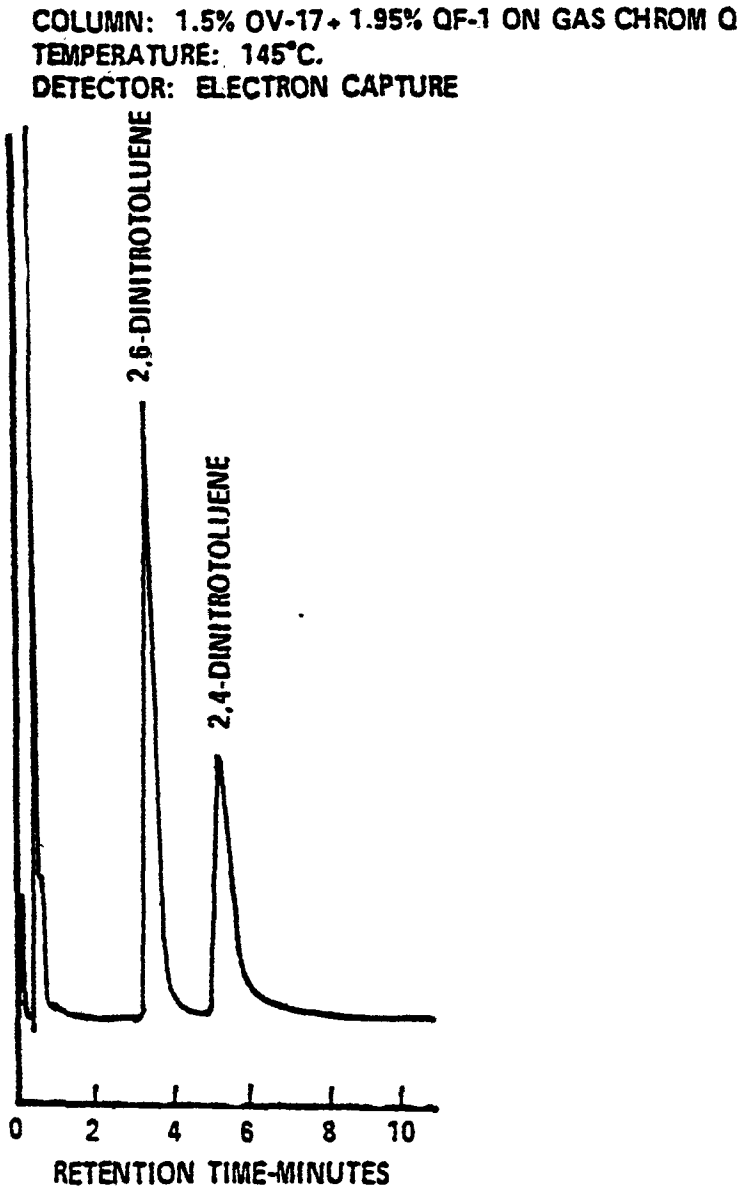


Figure 8.09-2
GAS CHROMATOGRAM OF DINITROTOLUENES

Method 8.10

GC AND HPLC METHODS FOR POLYNUCLEAR AROMATIC HYDROCARBONS

Scope and Application

This method covers the determination of certain polynuclear aromatic hydrocarbons (PAH). The following compounds may be determined by this method:

Benz(a)anthracene

Benz(b)fluoranthene

Chrysene

Creosote (Phenanthrene and Carbazole)

Naphthalene

This method contains both liquid and gas chromatographic approaches, depending upon the needs of the analyst. However, the gas chromatographic procedure cannot adequately resolve the following three pairs of compounds: Anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)-fluoranthene. If one wishes to resolve these pairs, the liquid chromatographic approach must be used for these compounds.

Summary of Method

Prior to using this method, the waste samples should be prepared for chromatography (if necessary) by using the appropriate sample preparation method (i.e., Shake Out, Sonication, or Soxhlet Extraction). This method provides chromatograpahic conditions which allow for the detection of the compounds in the extract by

either High Performance Liquid Chromatograph (HPLC) or gas chromatography.

If interferences are encountered, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials should be checked to insure freedom 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.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the waste sample. While a general clean-up technique is provided as part of this method, unique samples may require additional clean-up. The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed.

Apparatus

1. Kuderna-Danish (K-D) Apparatus equipped with the appropriate Snyder columns [Kontes K-570000 or equivalent]
2. Boiling chips - solvent extracted, approximately 10/40 mesh.
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. HPLC Apparatus:

a. Gradient pumping system, constant flow.

b. Reverse phase column, 5 micron HC-ODS Sil-X, 250 mm x 26 mm ID (Perkin Elmer No. 809-0716 or equivalent).

c. Fluorescence detector, for excitation at 280 nm and emission at 389 nm.

d. UV detector, 254 nm, coupled to fluorescence detector.

e. Strip chart recorder compatible with detectors. (A data system for measuring peak areas is recommended).

5. Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including dual flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

6. Chromatographic column - 250 mm long x 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

Reagents

1. Methylene chloride, pentane, cyclohexane, high purity water - HPLC quality, distilled in glass.

2. Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400° C for 4 hrs, in a shallow tray).

3. Stock standards - Prepare stock standard solutions at a concentration of 1.0 mg/ml by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution should be stored in a refrigerator, and checked

frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

4. Acetonitrile - Spectral quality.
5. Silica gel - 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hours at 130° C in a foil covered glass container.

Calibration

Prepare calibration standards that contain the compounds of interest, either singly or mixed together.

Assemble the necessary HPLC or gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 8.10-1 or 8.10-2. By injecting calibration standards adjust the sensitivity of the detectors and the analytical systems for each compound being analyzed for so as to detect $\leq$1 ug.

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.

Quality Control

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. The blank samples should be carried through all stages of the sample preparation and measurement steps.

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 samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug of contaminant/ gm of sample then the sensitivity of the instrument should be increased or the sample subjected to additional clean up. The fortified samples should be carried through all stages of the sample preparation and measurement steps.

Cleanup and Separation

(If the sample does not require cleanup, this section may be omitted.) Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane.

1. Add a 1-10 ml aliquot of sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube.
2. 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.
3. Place the micro-K-D apparatus on a boiling (100° C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood.

4. When the apparent volume of the liquid reaches 0.5 ml, remove K-D apparatus and allow it to drain for at least 10 minutes while cooling.
5. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane.
6. Adjust the extract volume to about 2 ml.

Silica Gel Column Cleanup for PAHs

1. Prepare a slurry of 10g activated silica gel in methylene chloride and place this in a 10 mm ID chromatography column. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1-2 cm of anhydrous sodium sulfate to the top of the silica gel.
2. Preelute the column with 40-ml pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 ml cyclohexane sample extract onto the column, using an additional 2 ml of cyclohexane to complete the transfer.
3. Just prior to exposure of the sodium sulfate layer to the air, add 25 ml pentane and continue elution of the column. Discard the pentane eluate.
4. Elute the column with 25 ml of 40% methylene chloride/60% pentane (v/v) and collect the eluate in a 500 ml K-D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml/minute.
5. Concentrate the collected fraction to less than 10 ml by K-D techniques, using pentane to rinse the walls of the glassware. Proceed with HPLC or gas chromatographic analysis.

High Performance Liquid Chromatography (HPLC)

1. To the extract in the concentrator tube, add 4 ml acetonitrile and a new boiling chip, then attach a micro-Snyder column. Increase the temperature of the hot water bath to 95-100° C. Concentrate the solvent to less than 0.5 ml. 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.
2. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with the compound of interest in order to insure a sensitivity of $\leq$ 1 ug. Table 8.10-1 summarizes the recommended HPLC column materials and instrument operating conditions. Included in this table are estimated retention times. An example of the separation achieved by this column is shown in Figure 8.10-1.
3. Inject 2-4 ml of the sample extract with a high pressure syringe or sample injection loop. Record the volume injected to the nearest 0.05 ml, and the resulting peak size, in area units.
4. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.
5. If measurement of the peak area measurement is prevented by the presence of interfering species, further cleanup is required.
6. The UV detector is recommended for the determination of napthalene and the fluorescence detector is recommended for

the remaining PAHs.

Gas Chromatography

The gas chromatographic procedure will not resolve certain isomeric pairs as was previously indicated. The liquid chromatographic procedure must be used for these materials.

1. To achieve maximum sensitivity with this method, the extract must be concentrated to 1.0 ml. Add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 ml of methylene chloride to the top. Place this micro-K-D apparatus on a hot water bath (60-65° C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 ml and stopper the concentrator tube.
2. Table 8.10-2 describes the recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are some estimated retention times

that should be achieved by this method. Table 8.10-3 indicates the appropriate chromatographic detectors. Calibrate the gas chromatographic system at the beginning and end of an analytical session by spiking aliquots of the extract with the compound of interest in order to insure a sensitivity of $\leq$ 1 ug.

3. Inject 2-5 ml of the sample extract using the solvent-flush technique. Smaller (1.0 ml) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ml, and the resulting peak size, in area units.

4. If the peak area measurement is prevented by the presence of interferences, further cleanup is required. If a response for the contaminant being analyzed for is greater than 2x background is noted; then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the method sensitivity is $\leq$ 1 ug of contaminant/gm of sample.

Table 8.10-1

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PAH'S

Compound	Retention time (min)
Naphthalene	16.17
Phenanthrene	22.32
Benzo(a)anthracene	29.26
Benzo(b)fluoranthene	32.44
Chrysene	30.14

Chromatographic conditions:

Reverse phase HC-ODS Sil-X 2.6 x 250 mm Perkin-Elmer column; isocratic elution for 5 minute using 40% acetonitrile/60% water, then linear gradient elution to 100% acetonitrile over 25 minutes; flow rate is 0.5 ml/minute.

Table 8.10-2

GAS CHROMATOGRAPHY OF PAH'S

Compound	Retention time (min)
Nephthalene	4.5
Phenanthrene	15.9
Benzo(a)anthracene	20.6
Benzo(b)fluoranthene	28.0
Chrysene	24.7

Chromatographic conditions:

Chromosorb W-AW-DCMs 100/120 mesh coated with 3% OV-17, packed in a 6' x 2 mm ID glass column, with nitrogen carrier gas at 40 ml/minute flow rate. Column temperature was held at 100° C for 4 minutes, then programmed at 8°/minute to a final hold at 280° C.

Table 8.10-3

APPROPRIATE GAS CHROMATOGRAPHIC DETECTORS

Compound	Detector
Benz(a)anthracene	FID
Benz(b)fluoranthene	FID
Carbazole	ECD
Chrysene	FID
Phenanthrene	ECD
Naphthalene	FID

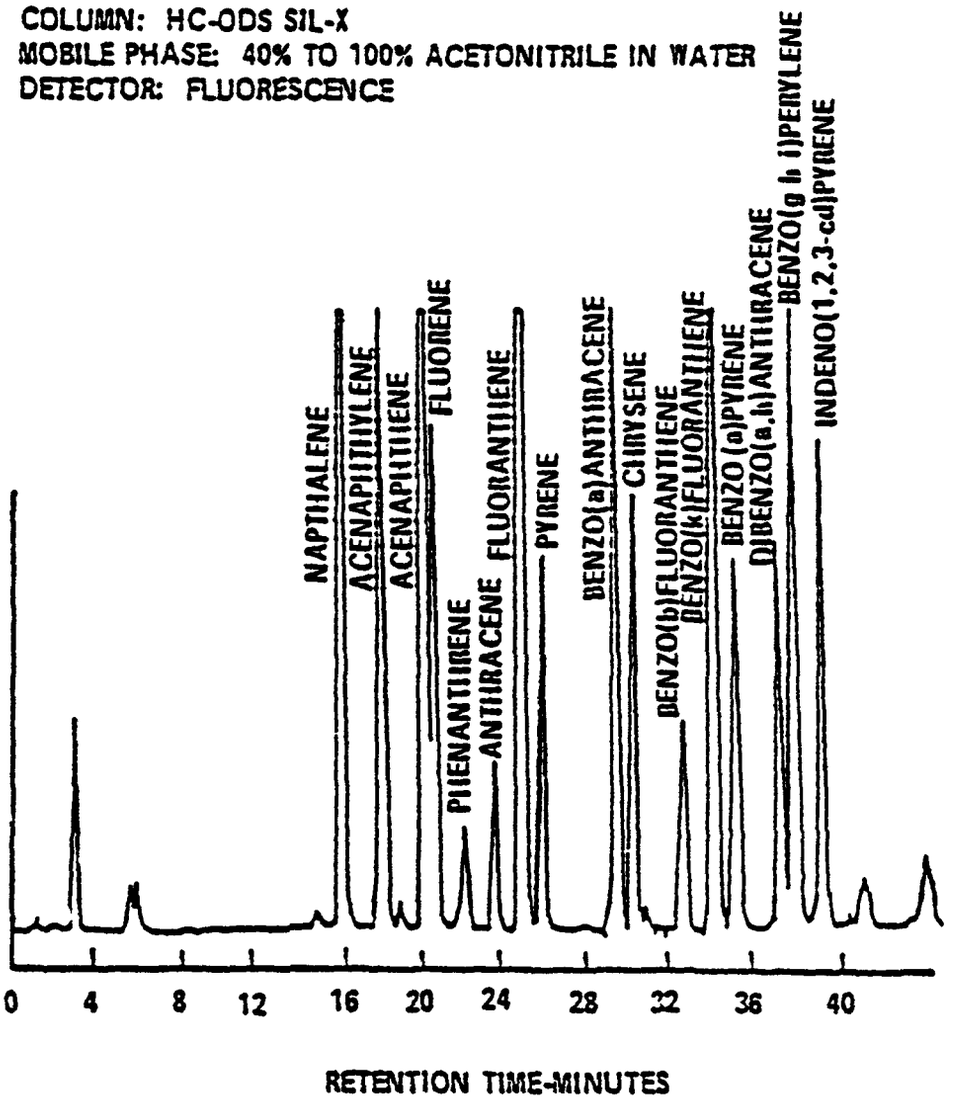


Figure 8.10-1

LIQUID CHROMATOGRAPHY OF POLYNUCLEAR AROMATICS

Method 8.12

GC METHOD FOR CHLORINATED HYDROCARBONS

Scope and Application

This method covers the determination of certain chlorinated hydrocarbons. The following compounds may be determined by this method.

Benzotrichloride

Benzyl Chloride

Dichlorobenzene

Dichloropropanol

Hexachlorobutadiene

Tetrachlorobenzene

Summary of Method

Prior to using this method, the waste samples are prepared for chromatography (if necessary) using the appropriate sample preparation method (i.e. shake out, sonication, or soxhlet extraction). This method describes chromatographic conditions which allow the accurate measurement of the compounds using electron capture detection.

If interferences are encountered or expected, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences

under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the waste being sampled. While general cleanup techniques are provided, unique samples may require additional cleanup.

Apparatus

1. Kuderna-Danish (K-D) Apparatus (Kontes K-570000 or equivalent).
   a. Snyder column-three-ball macro (Kontes K503000-0121 or eqivalent).
   b. Snyder column-two-ball micro (Kontes K503000-0219 or eqivalent).
2. Boiling chips-solvent extracted, approximately 10/40 mesh.
3. Water bath -heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.
4. Gas chromatograph-Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture detector column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.
5. Chromatography column-300 mm long x 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

Reagents

1. Methylene chloride, hexane isooctane and petroleum ether (boiling range 30-60°C)-pesticide quality or equivalent.
2. Sodium sulfate (ACS) granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).
3. Stock standards - Prepare stock standard solutions at a concentration of 10 ug/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.
4. Florisil-PR grade (60/100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil lined screw caps. Before use, activate each batch at 130°C in covered glass containers loosely covered with foil.

Calibration

1. Prepare calibration standards that contain the compounds of interest, either singly or mixed together.
2. Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 8.12-1. By injecting calibration

standards adjust the sensitivity of the detector and the analytical system for each compound being analyzed for to detect $\leq$ 1 ug.

3. The cleanup procedure utilizes Florisil chromatography. Florisil from different batches or sources may vary in adsorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this ratio by 110 and multiplying by 20 grams.
4. Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

Quality Control

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.

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 samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug/gm of the sample then the sensitivity of the instrument should be increased or the sample 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 chromatogram, confirmatory techniques such as mass spectroscopy should be used.

Cleanup and Separation

Unless the sample is known to require cleanup omit this section and proceed to analysis by gas chromatography.

1. Adjust the sample extract to 10 ml.
2. Place a 12 gram charge of activated Florisil in a 10 mm ID chromatography column. After settling the Florisil by tapping the column add a 1-2cm layer of anhydrous granular sodium sulfate to the top.
3. Pre-elute the column, after cooling, with 100 ml of petroleum ether. Discard the eluate and just prior to

exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 ml petroleum ether and collect the eluate in a 500 ml K-D flask equipped with a 10 ml concentrator tube. This fraction should contain all of the chlorinated hydrocarbons.

4. Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml hexane to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1-2ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Note: The dichlorobenzenes have a sufficiently high volatility that significant losses may occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1-2ml before

removing the K-D from the hot water bath. 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.

5. Transfer to a 10 ml volumetric flask and dilute to volume.

Gas Chromatography

1. Table 8.12-1 lists the recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are some estimated retention times. Examples of the separations achieved by this column are shown in Figures 1 and 2. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the sample being analyzed with the compound of interest in order to insure a sensitivity of (1 ug/gm) of original waste or extract tested.
2. Inject 2-5 ul of the sample extract using the solvent flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed.
3. If the peak area exceeds the linear range of the system the extract can be diluted and reanalyzed.
4. If peak detection is prevented by the presence of interferences, further cleanup is required. If detectable amounts of the compounds of interest are detected the waste does not meet the criteria for delisting of being fundamentally different from that of the listed waste.

Calculations

1. If a response for the contaminant being analyzed for greater than 2x background is noted, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm of sample.

Bibliography

1. Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51,29 (1968).

Table 8.12-1

RETENTION TIMES FOR SOME CHLORINATED HYDROCARBONS

Compound	Retention time (min)[1]
1, 3 dichlorobenzene	4.0
1, 4 dichlorobenzene	4.3
1, 2 dichlorobenzene	5.3
Hexachlorobutadiene	11.6
Benzotrichloride	
Benzyl chloride	
Dichloropropanol	
Tetrachlorobenzene(s)	

(1) Gas chrom Q, 80/100 mesh, coated with 1.5% OV-1/1.5% OV-225 packed in a 1.8 m long x 2 mm ID glass column with 5% methane/95% Argon carrier gas at 30 ml/min flow rate. Column temperature is 75°C. Under these conditions Retention Time of Aldrin is 18.8 min at 160°C.

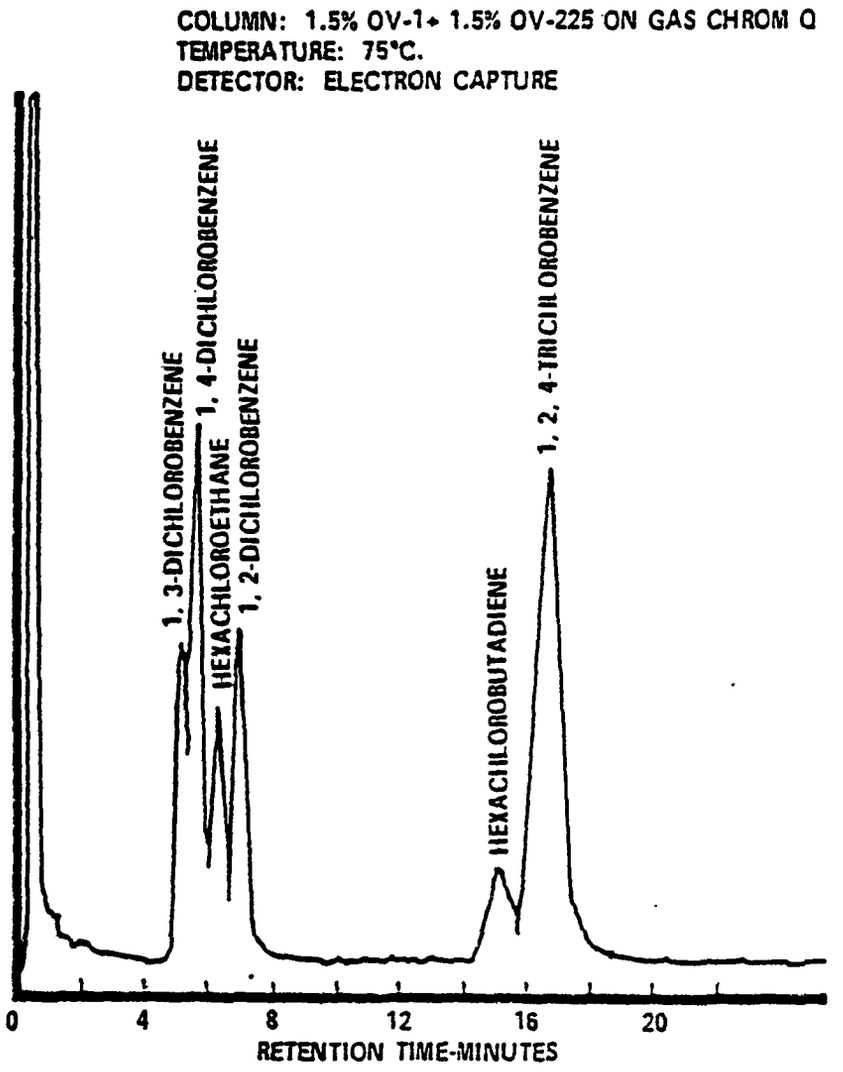


Figure 8.12-1
GAS CHROMATOGRAM OF CHLORINATED HYDROCARBONS

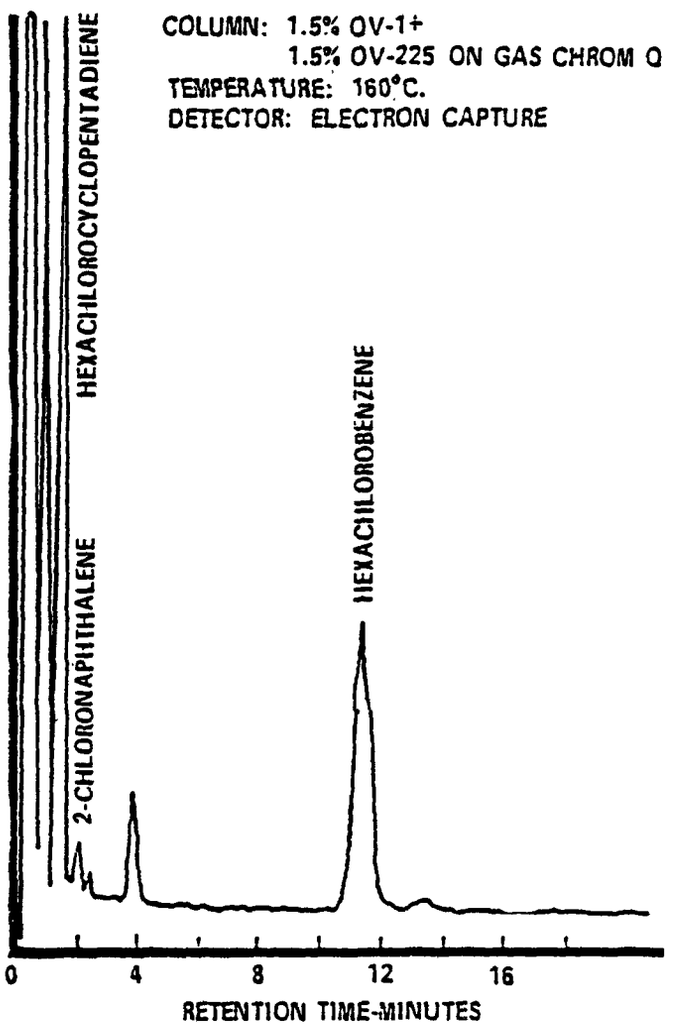


Figure 8.12-2
GAS CHROMATOGRAM OF CHLORINATED HYDROCARBONS

Method 8.22

PHORATE

Scope and Application

This method covers the determination of the presence of phorate in RCRA materials.

Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method (i.e., shake out, sonication, or soxhlet extration).

Summary of Method

This method provides chromatographic conditions which allow for the detection of the compounds in the extract.

The detector of choice is the flame photometric detector operated in the phosphorus mode. A thermionic detector operated in the phosphorus-nitrogen mode may also be used.

If interferences are encountered, it may be necessary to apply cleanup procedures.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the

diversity of the waste sample. Unique samples may require clean-up to achieve the required sensitivity in which case the analyst must devise appropriate cleanup procedures.

Elemental sulfur may interfere with the determination of organophosphorus pesticides by flame photometric gas chromatography.

Apparatus

1. Gas chromatograph-Analytical system complete with gas chromatograph suitable for on-column injection and programmed temperature operation. Required accessories include: A flame photometric or phosphorous-nitrogen detector, column supplies, recorder, gases, and syringes. A data system for measuring peak areas is recommended. A 6 foot long x 4mm ID glass column packed with 5% SP-2401 on 100/120 mesh Supelcoport shall be used.

Reagents

1. Hexane, isooctane, methylene chloride - pesticide quality or equivalent.
2. Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul by dissolving 0.0100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 10.0 ml ground glass stoppered volumetric flask. Transfer the stock solution to a small glass vial and seal with a Teflon lined screw cap and store in a refrigerator. Check frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

Calibration

1. Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The secondary standards should be prepared at concentrations that will bracket the working range of the chromatographic system.
2. Establish operating parameters equivalent to those indicated on Figure 8.22-1. By injecting calibration standards, adjust the limit of the detection so as to detect $\leq$ 1 ug of phorate.

Quality Control

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 safequard against chronic laboratory contamination.
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 of waste should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectrometry should be used.

Procedure

1. The recommended gas chromatographic column materials and operating conditions for the instrument are described under "Apparatus" and on Figure 8.22-1. The retention time for phorate using this column is 1.43 min. An example chromatogram for phorate and other organophosphorus pesticides is shown in Figure 8.22-1. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with phorate in order to insure an analytical sensitivity of $\leq$ 1 ug/gm of original waste tested.
2. Inject 2 to 5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.
3. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.
4. If peak detection is prevented by the presence of interferences, further cleanup is required.

Results

If a response for the contaminant being analyzed for is greater than 2x background is noted; then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the method sensitivity is $\leq$ 1 ug of phorate/gm of sample.

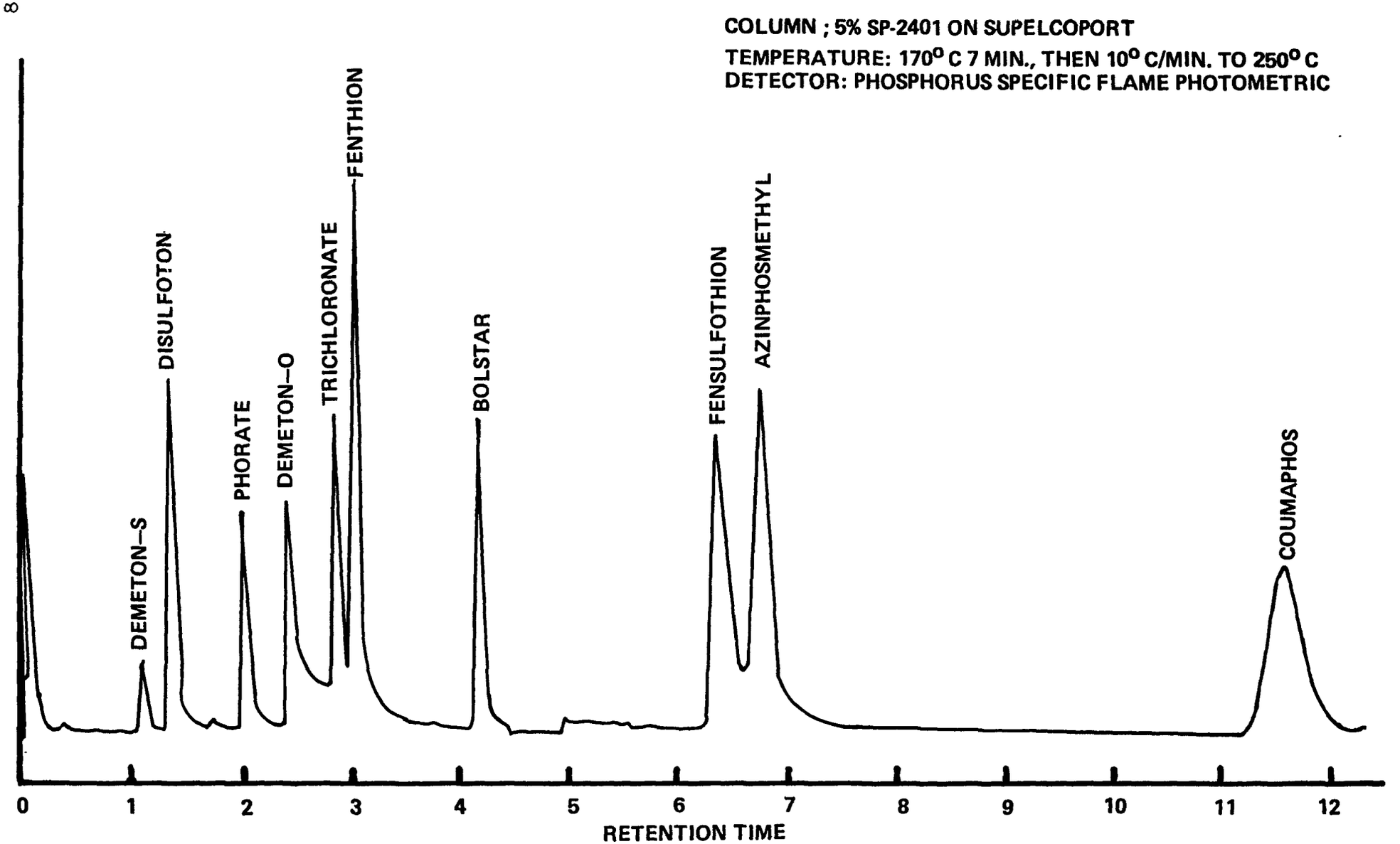


Figure 8.22-1

GC CHROMATOGRAM OF ORGANOPHOSPHORUS PESTICIDES

Method 8.40

METHOD FOR CHLOROPHENOXY ACID HERBICIDES

Scope and Application

This method can be used for the determination of various chlorinated phenoxy acid herbicides in EP extracts and other RCRA materials.

The following pesticides may be determined individually by this method:

Compound	Detector
Dichlorophenoxy acetic acid	HSD
2,4,5-TP (Silvex) [2,4,5-Trichlorophenoxy proponic acid]	HSD

Summary of Method

Prior to using this method, the waste samples should be prepared for chromatography, if necessary, using the appropriate sample preparation method (i.e., Sonication or Soxhlet extraction). The esters are hydrolyzed to acids and extraneous organic material is removed by a solvent wash. The acids are converted to methyl esters which are extracted from the aqueous phase. The extract is cleaned by passing it through a micro-adsorption column. Identification of the esters is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

Interferences

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials should be checked to insure freedom from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

The interferences in extracts of solid waste are often high and varied and may pose great difficulty in obtaining accurate and precise measurement of chlorinated phenoxy acid herbicides. Sample cleanup procudures are generally required and may result in loss of certain of these herbicides. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in solid waste samples.

Organic acids, especially chlorinated acids, cause the most direct interferences with the determination. Phenols including chlorophenols will also interfere with this procedure.

The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Glassware and glass wool should be acid-rinsed and sodium sulfate should be acidified with sulfuric acid to avoid this possiblity.

Apparatus

1. Gas Chromatograph - Equipped with glass lined injection port.
2. Detector Options:

a. Electron Capture - Radioactive (Tritium or Nickel-63)

b. Microcoulometric Titration

c. Electrolytic Conductivity

3. Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4. Gas Chromatographic Column Materials

a. Tubing - pyrex (180 cm long x 4 mm ID)

b. Glass Wool - Silanized

c. Solid Support - Gas-Chrom-Q (100-120 mesh)

d. Liquid Phase - Expressed as weight percent coated on solid support.

i. OV-210,5%

ii. OV-17, 1.5% plus QF-1 or OV-210, 1.95%

5. Kuderna-Danish (K-D) Glassware

a. Snyder Column - three-ball (macro) and two-ball (micro)

b. Evaporative Flasks - 250 ml

c. Receiver Ampules - 10 ml, graduated

d. Ampule Stoppers

6. Blender - High speed, glass or stainless steel cup.

7. Graduated cylinders - 100 ml and 250 ml.

8. Erlenmeyer flasks - 125 ml, 250 ml ground glass 24/40

9. Microsyringes - 10, 25, 50 and 100 l.

10. Pipets - Pasteur, glass disposable (140 mm long x 5 mm ID).

11. Separatory Funnels - 60 ml and 2000 ml with Teflon stopcock.

12. Glass wool - Filtering grade, acid washed.

13. Diazald Kit - Recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. #210,025-2)

Reagents

1. Boron Trifluoride-methanol-esterification-reagent, 14 percent boron trifluoride by weight.
2. N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald) - High purity, melting point range 60-62°C. Precursor for the generation of diazomethane (see Appendix IV).
3. Potassium Hydroxide Solution - A 37 percent aqueous solution prepared from reagent grade potassium hydroxide pellets and reagent water.
4. Sodium Chloride - (ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.
5. Sodium Hydroxide - (ACS) 10 N in distilled water.
6. Sodium Sulfate, Acidified - (ACS) granular sodium sulfate, treated as follows: Add 0.1 ml of concentrated sulfuric acid to 100g of sodium sulfate slurried with enough ethyl ether to just cover the solids. Remove the ether with the vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and ensure the mixture has a pH below 4. Store at 130°C.
7. Sulfuric Acid - (ACS) concentrated, Sp. Gr. 184
8. Florisil - PR grade (600-100 mesh) purchased activated at 1250°F and stored at 130°C.
9. Carbitol (diethylene glycol monoethyl ether).
10. Diethyl Ether - Nanograde, redistilled in glass, if necessary.
    a. 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.) Procedures recommended for removal of peroxides are provided with the test strips.

11. Benzene, hexane - Nanograde, redistilled in glass, if necessary.

12. Pesticide Standards - Acids and methyl esters, reference grade.

    a. Stock standard solutions - Dissolve 100 mg of each herbicide in 60 ml ethyl ether; then make to 100 ml with redistilled hexane. Solution contains 1 mg/ml.

    b. Working standard - Pipet 1.0 ml of each stock solution into a single 100 ml volumetric flask. Make to volume with a mixture of ethyl ether and hexane (1:1). Solution contains 10 ug/ml of each standard.

    c. Standards for Chromatography (Diazomethane Procedure) - Pipet 1.0 ml of the working standard into a glass stoppered test tube and evaporate the solvent using a steam bath. Add 2 ml diazomethane to the residue. Let stand 10 minutes with occasional shaking, then allow the solvent to evaporate spontaneously. Dissolve the residue in 200 ul of hexane for gas chromatography.

    d. Standard for Chromatography (Boron Trifluoride Procedure) - Pipet 1.0 ml of the working standard into a glass stoppered test tube. Add 0.5 ml

of benzene and evaporate to 0.4 ml using a two-ball Snyder microcolumn and a steam bath. Proceed as in the Esterification section (3)(a). Esters are then ready for gas chromatogrphy.

Calibration

1. By injecting secondary standards, adjust the sensitivity limit and the linear range of the analytical system for each compound being analyzed for to a sensitivity of $\leq$ 1 ug (2 x background).
2. Standards, prepared from methyl esters of phenoxy acid herbicides calculated as the acid equivalent are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several chlorophenoxys are shown in Figure 8.40-1.
3. The elution order and retention ratios of methyl esters of chlorinated phenoxy acid herbicides are provided in Table 8.40-1, as a guide.

Quality Control

1. Duplicate and spiked sample analyses are recommended as quality control checks. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.
2. Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

Hydrolysis

1. Add 15 ml of distilled water and a small boiling stone to

the flask containing the ether extract (prepared by approriate sample preparation method) and fit the flask with a three-ball Snyder column. Evaporate the ether in a steam bath and continue heating for a total of 60 minutes.

2. Transfer the concentrate to a 60-ml separatory funnel.
3. Acidify the contents of the separatory funnel by adding 2 ml of cold (4°C) 25 percent sulfuric acid. Extract the herbicides once with 20 ml of ether and twice with 10 ml of ether. Collect the extracts in a 125 ml Erlenmeyer flask containing about 0.5 g of acidified anydrous sodium sulfate. Allow the extract to remain in contact with the sodium sulfate for approximately two hours.

Esterification

1. Transfer the ether extract through a funnel plugged with glass wool into a Kuderna-Danish flask equipped with a 10 ml graduated ampule. Use liberal washings of ether. Using a glass rod crush any caked sodium sulfate during the transfer.
   a. If esterification is to be done with diazomethane, evaporate to approximately 4 ml on a steam bath (do not immerse the ampule in water) and proceed as directed under "Diazomethane Esterification". Prepare diazomethane as directed in manufacturer's instructions.
   b. If esterification is to be done with boron trifluoride, add 0.5 ml benzene and evaporate to about 5 ml on a steam bath. Remove the ampule from the flask and further concentrate the extract to 0.4 ml using a

two-ball Snyder microcolumn and proceed as directed under "Boron Trifluoride Esterification.

2. Diazomethane Esterification:

   a. Disconnect the ampule from the K-D flask and place in a hood away from steam bath. Adjust volume to 4 ml with ether, add 2 ml diazomethane, and let stand 10 minutes with occasional swirling.

   b. Rinse inside wall of ampule with several hundred microliters of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature).

   c. Dissolve residue in 5 ml of hexane. Analyze by gas chromatography.

   d. If further cleanup of the sample is required, proceed as in 3(c), substituting hexane for benzene.

3. Boron Trifluoride Esterification:

   a. After the benzene solution in the ampule has cooled, add 0.5 ml of borontrifluoride-methanol reagent. Use the two-ball Snyder microcolumn as an air-cooled condenser and hold the contents of the ampule at 50°C for 30 minutes on the steam bath.

   b. Cool and add about 4.5 ml of a neutral 5 percent aqueous sodium sulfate solution so that the benzene-water interface is in the neck of the Kuderna-Danish ampule. Seal the flask with a ground glass stopper and shake vigorously for about one minute. Allow

to stand for three minutes for phase separation.

c. Pipet the solvent layer from the ampule to the top of a small column prepared by plugging a disposable Pasteur pipet with glass wool and packing with 2.0 cm of sodium sulfate over 1.5 cm of Florisil adsorbent. Collect the elute in in a graduated ampule. Complete the transfer by repeatedly rinsing the ampul with small quantities of benzene and passing the rinses through the column until a final volume of 5.0 ml of eluate is obtained. Analyze by gas chromatography.

Calculation and Results

In analyzing EP extracts to determine if a waste is a hazardous waste by reason of EP toxicity, calculate results in milligrams per liter as the acid equivalent after correcting for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

In determining if a waste should be delisted, if a response for the contaminant being analyzed for greater than 2 x background is noted, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using that spiked samples, that the instrument sensitivity is $\leq$ lug of contaminant /gm of sample.

Method 8.24

GC/MS METHOD FOR VOLATILE ORGANICS

Scope and Application

This method is designed to determine volatile organic compounds.

Summary of Method

The volatile compounds are introduced to the gas chromatograph by direct injection (Method 8.80), the Headspace Method (Method 8.82) or the Purge and Trap Method (Method 8.83). 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.

Interferences

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 insure 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.

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.

Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

Apparatus and Materials

1. Gas chromatograph--Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.
   a. Column 1--An 8 ft. stainless steel column (.125 in. OD x 2 mm ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceeded by a 1 ft. stainless steel column (.125 in. OD x 2mm ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. A glass column .25 i x 2mm ID may be substituted for the stainless steel. The

glass precolumn is necessary only during conditioning.

b. Column 2--An 8 ft. stainless steel column (.125 in. OD x 2 mm ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (.125 in. OD x 2 mm ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (1/4 in. OD x 2mm ID) may be substituted for the stainless steel. The precolumn is necessary only during conditioning.

2. Syringes--glass, 5 ml hypodermic with Luer-Lok tip (3 each).

3. Micro syringes--10, 25, 100 ul.

4. 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

5. Syringe--5 ml gas-tight with shut-off valve.

6. 8-inch, 20 gauge syringe needle--one needle for each 5-ml syringe.

7. Mass Spectrometer--capable of scanning from 20-260 a.m.u. in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any

separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 8.24-1.

8. A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There must be computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

Reagents

1. Activated carbon--Filtrasorb-200 (Calgon Corp.) or equivalent.
2. Organic-free water.
   a. Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing distilled deionized water through a carbon filter bed containing activated carbon.
   b. A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.
   c. Organic-free water may also be prepared by boiling deionized distilled water 15 minutes. Subsequently,

while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

3. Stock standards (2 mg/ml)--Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

   a. Place about 9.8 ml of methanol into a 10 ml ground glass stopped volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

   b. Add the assayed reference material:

      Liquids--using a 100 ul syringe, immediately add 2 to 3 drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

      Gases--To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a 5-ml valved gas-tight syringe with the reference standard to the 5.0 ml mark. Lower the needle to 5 mm above the methyl alcohol menicus. Slowly inject

the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

c. Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle equipped with a Teflon cap liner.

d. Calculate the concentration in mg per ml (equivalent to ug per ul) from the net gain in weight.

e. Store stock standards at 4°C. Prepare fresh standards every second day for the four gases and 2-chloroethyl-vinyl ether. All other standards must be replaced with fresh standards each week.

4. Surrogate Standard Dosing Solution--From stock standard solutions prepared as above, add a volume to give 1000 ug each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50 ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5 ml sample and reference standard analyzed.

Calibration

1. Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The aqueous standards must be prepared fresh daily. Standards should be at concentrations such that the aqueous standards to be prepared will bracket the working range of the chromatographic system. If the limit of detection listed in Table 8.24-1 is 10 ug/l, for example, prepare secondary methanolic standards at 100 ug/l, and 500 ug/l, so that aqueous standards prepared from the secondary calibration standards, and the primary standards will define the linearity of the detector in the working range.
2. Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 8.24-1. By injecting secondary dilution standards, adjust the sensitivity of the analytical system for each compound to $\leq$1 ug.

Quality Control

1. Before processing any samples, the analyst should daily demonstrate through the analysis of an organic-free water method blank, that the entire analytical system is interference-free. The blank samples should be carried through all stages of the sample preparation and measurement steps.

2. Standard quality assurance as indicated in Section 10 should be followed. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates and fortified samples should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect $\leq$ 1 ug/gm of sample then the sensitivity of the instrument should be increased or the sample subjected to additional clean up. The fortified samples should be carried through all stages of the sample preparation and measurement steps.
3. The analyst should maintain constant surveillance of both the performance of the analytical system and the effectivenesss of the method in dealing with each sample matrix.

Gas Chromatography-Mass Spectrometry

1. Table 8.24-1 summarizes the recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are some estimated retention times. An example of the separation achieved by Column 1 is shown in Figure 8.24-4.
2. GC-MS Determination--Suggested analytical conditions are given below. Operating conditions vary from one system to another, therefore, each analyst must optimize the conditions for his particular GC/MS system.

3. Mass Spectrometer Parameters:

   Electron energy--70 volts (nominal).

   Mass range--20-27, 33-260 amu.

   Scan time--6 seconds or less.

4. Calibration of the gas chromatography-mass spectrometry GC-MS system--Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass specrum of DFTPP or BFB.

   a. To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP-2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 8.24-2 are met.

   b. To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 8.24-3 are met.

   c. If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

5. Analyze an internal or external calibration standard to develop response factors for each compound.

Quantitative Determination

1. To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table

8.24-4. The criteria below must be met for a quantitative identification.

a. The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

b. The retention time at the experimental mass spectrum must be within 60 seconds of the retention time of the authentic compound.

c. The ratios of the three EICP peak heights must agree with ± 20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC-MS system or from a reference library.

d. Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise structural isomers are identified as isomeric pairs.

2. The primary ion listed in Table 8.24-4 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

3. For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses

listed for the compounds in Table 8.24-4 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

Results

If a response for the contaminant being analyzed for greater than 2 X background is noted, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm of sample.

References

1. "The Analysis of Halogenated Chemical Indicators of Industrial Contamination in Water by the Purge and Trap Method," U.S. EPA, Environmental Monitoring and Support Laboratory, Cincinnati, OH, 45268, Dec. 1978.

2. Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography," T.A. Bellar and J.J. Lichtenberg, Jour. AWWA, 66, 739-744, Dec. 1974.

3. ASTM Annual Standards--Water, Part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

4. "Direct Analysis of Water Samples for Organic Pollutants with Gas Chromatography-Mass Spectrometry," Harris, L.E., Budde, W.L., and Eichelberger, J.W. Anal. Chem., 46, 1912 (1974).

5. "Sampling and Analysis Procedures for Screening of Industrial Effluents for Priority Pollutants," March 1977 (revised April 1977). USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

6. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1 - Denver, Colorado, November 1977; Volume 2 - Savannah, Georgia, May 1978; Volume 3 - Norfolk, Virginia, March 1979; USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 8.24-1

GAS CHROMATOGRAPHY OF ORGANICS

Compound	Retention Time (min) Column 1	Column 2
chloromethane	1.50	2.10
vinyl chloride	2.67	2.57
trichlorofluoromethane	7.18	5.14
1,1-dichloroethane	9.30	6.48
chloroform	10.68	7.70
1,2-dichloroethane	11.40	8.29
1,1,1-trichloroethane	12.60	9.28
carbon tetrachloride	13.02	9.45
trichloroethene	15.80	11.98
1,1,2-trichloroethane	16.52	12.86
benzene	---	12.95
1,1,2,2-tetrachloroethane	21.62	17.70
tetrachloroethene	21.67	17.44
toluene	---	18.53
chlorobenzene	24.18	20.57
acrolein		
acrylonitrile		

Column 1 Eight ft. stainless steel column (.125 in OD x 0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 1 ft. stainless steel column (.125 in. OD x 0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. (A glass column (.25 in. OD x 2 mm ID) may be substituted). Carrier gas helium at 40 ml/min. Temperature program: 3 min isothermal at 45°C, then 8°/min to 220°, hold at 220° for 15 minutes.

Column 2 Eight ft. stainless steel column (.125 in. OD x 0.1 in ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (.125 in. OD x 0.1 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. (A glass column (.25 in. OD x mm ID) may be substituted. Carrier gas: helium at 40 ml/min. Temperature program: 3 min isothermal at 60°C then 8°/min to 160°, hold at 160 until all compounds elute.

Table 8.24-2

DFTPP KEY IONS AND ION ABUNDANCE CRITERIA

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

Table 8.24-3

BFB KEY IONS AND ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	20-40% of mass 95
75	50-70% mass 95
95	base peak, 100% relative abundance
96	5-9% of mass 95
173	less than 1% of mass 95
174	70-90% of mass 95
175	5-9% of mass 95
176	70-90% of mass 95
177	5-9% of mass 95

Table 8.24-4

CHARACTERISTIC IONS OF VOLATILE ORGANICS

Compound	E I Ions				Primary Ion
chloromethane	50	52			50
vinyl chloride	62	64			62
trichlorofluoromethane	101	103			101
1,1-dichloroethane	63	65	83		63
	85	98	100		
chloroform	83	85			83
1,2-dichloroethane	62	64	98	100	98
1,1,1-trichloroethane	97	99	177	199	
carbon tetrachloride	117	119	121		117
trichloroethene	95	97	130	132	130
1,1,2-trichloroethane	83	85	97		
	99	132	134		97
benzene	78				78
	252	254	256		
tetrachloroethene	129	131	164	166	164
1,1,2,2-tetrachloroethane	83	85	131	133	
	166	168			168
toluene	91	92			92
chlorobenzene	112	114			112
acrolein	26	27	55	56	56
acrylonitrile	26	51	52	53	53

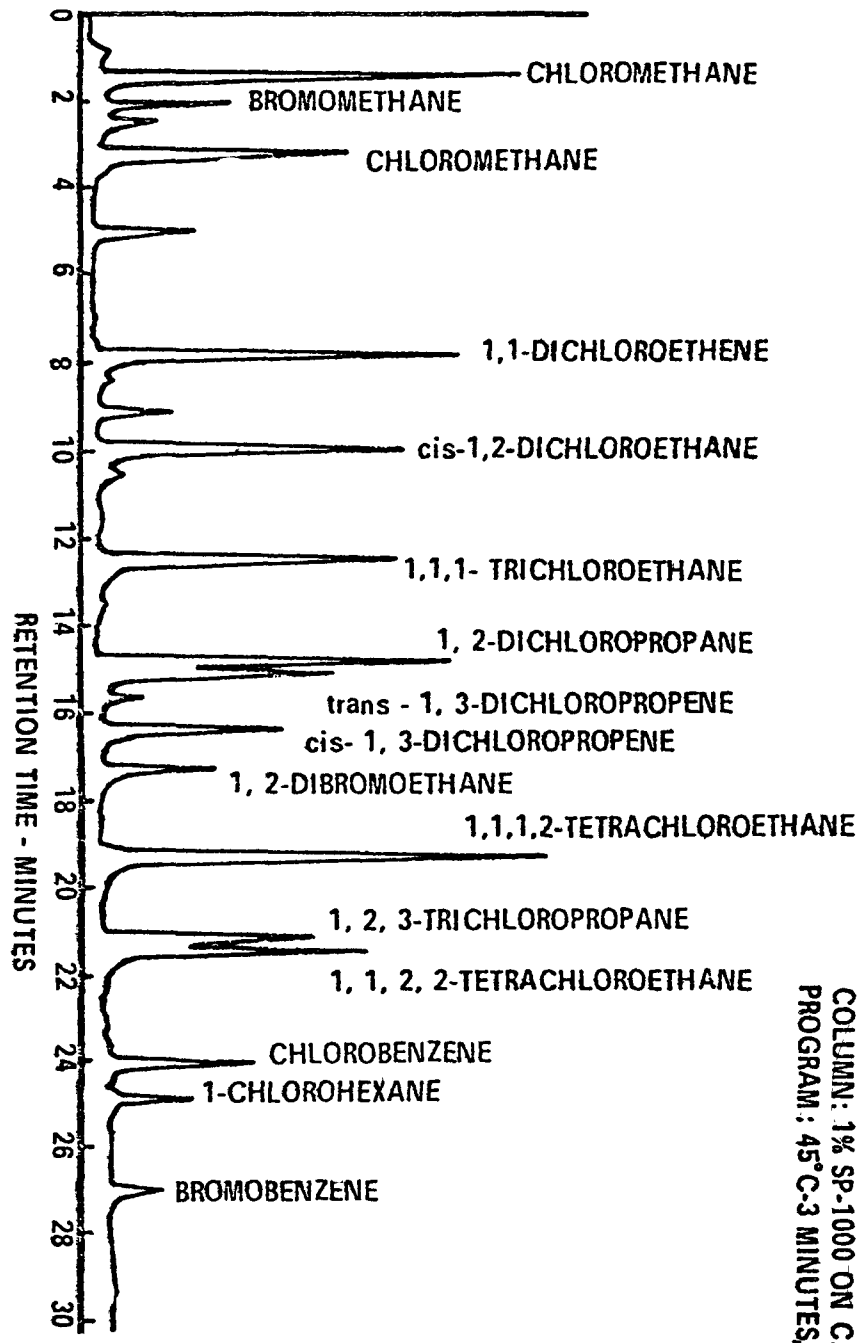


Figure 8.24-1
GAS CHROMATOGRAM OF VOLATILE ORGANICS BY PURGE AND TRAP

Method 8.25

GC/MS METHOD, GENERAL

Scope and Application

The following compounds may be determined by this method:

Benzo(a)anthracene

Benzo(a)pyrene

Benzotrichloride

Benzyl chloride

Benzo(b)fluoranthene

Chlordane

Chlorinated dibenzodioxin

Chlorinated biphenyls

2-Chlorophenol

Chrysene

Creosote

Cresol(s)

Cresylic acid(s)

Dichlorobenzene(s)

Dichlorophenoxyacetic acid

Dichloropropanol

2,4-Dimethylphenol

Dinitrobenzene

4,6-Dinitro-o-cresol

2,4-Dinitrotoluene

Endrin

Formic acid

Heptachlor

Hexachlorobenzene

Hexachlorobutadiene

Hexachloroethane

Hexachlorocyclopentadiene

Lindane

Maleic anhydride

Methyl ethyl ketone

Methyl isobutyl ketone

Naphthalene

Napthoquinone

Nitrobenzene

Pentachlorophenol

Phenol

Phthalic anhydride

2-Picoline

Pyridine

Tetrachlorobenzene(s)

Toluenediamine

Toluene diisocyanate(s)

Toxaphene

Trichlorophenol(s)

2,4,5-TP(Silvex)

Summary of Method

Prior to using this method, the waste samples should be prepared for chromatography (if necessary) using the appropriate sample preparation method (i.e., shake out, sonication, or soxhlet extraction). 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.

Interferences

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or waste being sampled.

The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene, and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. If identification of these specific compounds is required Method 8.10 should be used.

Apparatus

1. Separatory funnel - 20 mm, with Teflon stopcock (Ace Glass 7228-T072 or equivalent).

2. Drying column - 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.
3. Kuderna-Danish (K-D) Apparatus equipped with 3-ball Snyder column (Kontes K-570000 or equivalent).
4. Water bath - Heated with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.
5. Gas chromatograph - Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.
6. Column 1 - For Base/Neutral and Pesticides a 6-foot glass column (1/4 in OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 Supelcoport (or equivalent).
7. Column 2 - For Acids, a 6-foot glass column (1/4 in OD x 2mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport (or equivalent).
8. Mass Spectrometer - Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (References 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or

glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note: - Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives recognizable mass spectra and acceptable calibration points at the required limit of detection.

9. A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There must be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential if quantification is to be attempted.
10. Continuous liquid-liquid extractors-Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor-Ace Glass Co., Vineland, N.J. P/N 6841-10 or eqivalent).

Reagents

1. Sodium hydroxide - (ACS) 6N in distilled water.
2. Sulfuric acid - (ACS) 6N in distilled water.

3. Sodium sulfate - (ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400°C for 4 hrs.).
4. Methylene chloride - Pesticide quality or equivalent.
5. Stock standards - Prepare stock standard solutions at a concentration of 1.00 ug/ul. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator, and checked frequently for signs of degradation of evaporation, especially just prior to preparing working standards from them. Protect standards from light.

Procedure

1. Calibrate instrument using the conditions indicated in Table 8.25-1, so that a response greater than 2 times background is obtained for 1 ug of each species being analyzed for.
2. Inject the extract derived from 1 gm of the sample being analyzed. The extract should be diluted and range finding studies conducted prior to injection of concentrated extract in order to prevent instrument overload.

Results

If a response for the contaminant being analyzed for is greater than 2x background is noted; then the waste does not

meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm of sample.

Quality Control

1. Before processing any samples, demonstrate through the analysis of a method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.
2. Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

Table 8.25-1

CHROMATOGRAPHIC CONDITIONS

Benz(a)anthracene	BN
Benzo(a)pyrene	BN
Benzotrichloride	BN
Benzyl chloride	BN
Benz(b)fluoanthene	BN
Chlordane	BN
Chlorinated dibenzodioxin	BN
Chlorinated biphenyls	BN
2-Chlorophenol	BN
Chrysene	BN
Creosote	BN
Cresol(s)	A
Cresylic acid(s)	A
Dichlorobenzene(s)	BN
Dichlorophenoxyacetic acid	A
Dichloropropanol	BN
2,4-Dimethylphenol	A
Dinitrobenzene	BN
4,6-Dinitro-o-cresol	A
2,4-Dinitrotoluene	BN
Endrin	P
Formic acid	BN
Heptachlor	P
Hexachlorobenzene	BN
Hexachlorobutadiene	BN
Hexachloroethane	BN
Hexachlorocyclopentadiene	BN
Lindane	P
Maleic anhydride	BN
Methyl ethyl ketone	A
Methyl isobutyl ketone	A
Naphthalene	BN
Napthoquinone	BN
Nitrobenzene	B
Pentachlorophenol	A
Phenol	BN
Phthalic anhydride	BN
2-Picoline	BN
Pyridine	BN

Table 8.25-1 (Cont.)

Tetrachlorobenzene(s)	BN
Toluenediamine	BN
Toluene diisocyanate(s)	BN
Toxaphene	P
Trichlorophenol(s)	A
2,4,5-TP(Silvex)	A

(A) °8 foot glass column (1/4 in. OD x 2 mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport. Carrier gas helium at 30 ml per min. Temperature program: 2 min isothermal at 70°, then 8° per min to 200°C. If desired, capillary or SCOT columns may be used.

(BN) #Six foot glass column (1/4 in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas helium at 30 ml per min. Temperature program: isothermal for 4 minutes at 50°C, then 8° per min to 270°C. Hold at 270°C for 30 minutes. If desired, capillary or SCOT columns may be used.

(P) °6 foot glass column (1/4 in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Superlcoport. Carrier gas helium at 30 ml per min. Temperature program: isothermal for 4 minutes at 50°C, then 8° per minute to 270°. Hold at 270°C for 30 minutes. If desired, capillary or SCOT columns may be used

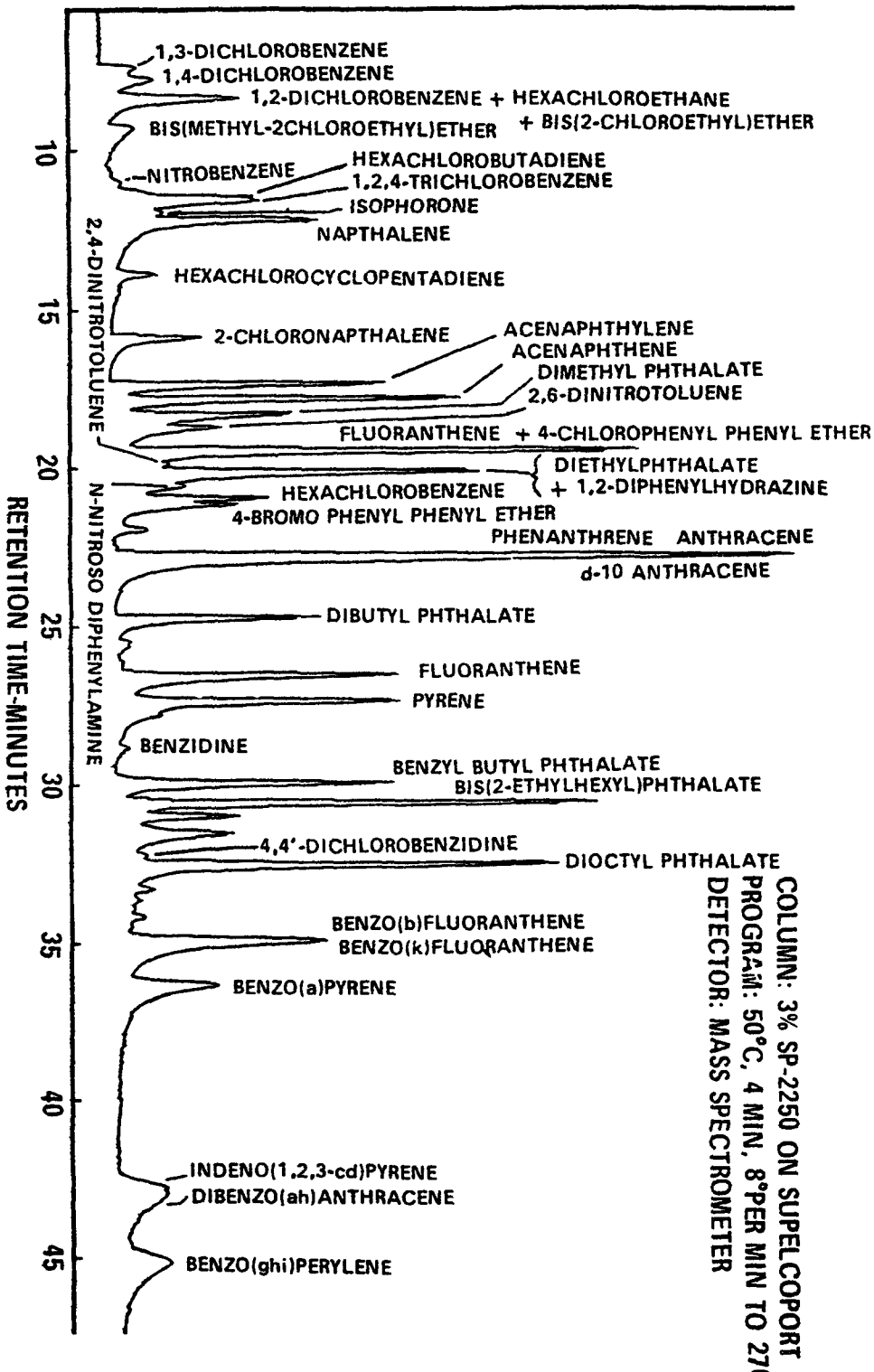


Figure 8.25-1
GAS CHROMATOGRAM OF BASE/NEUTRAL FRACTION

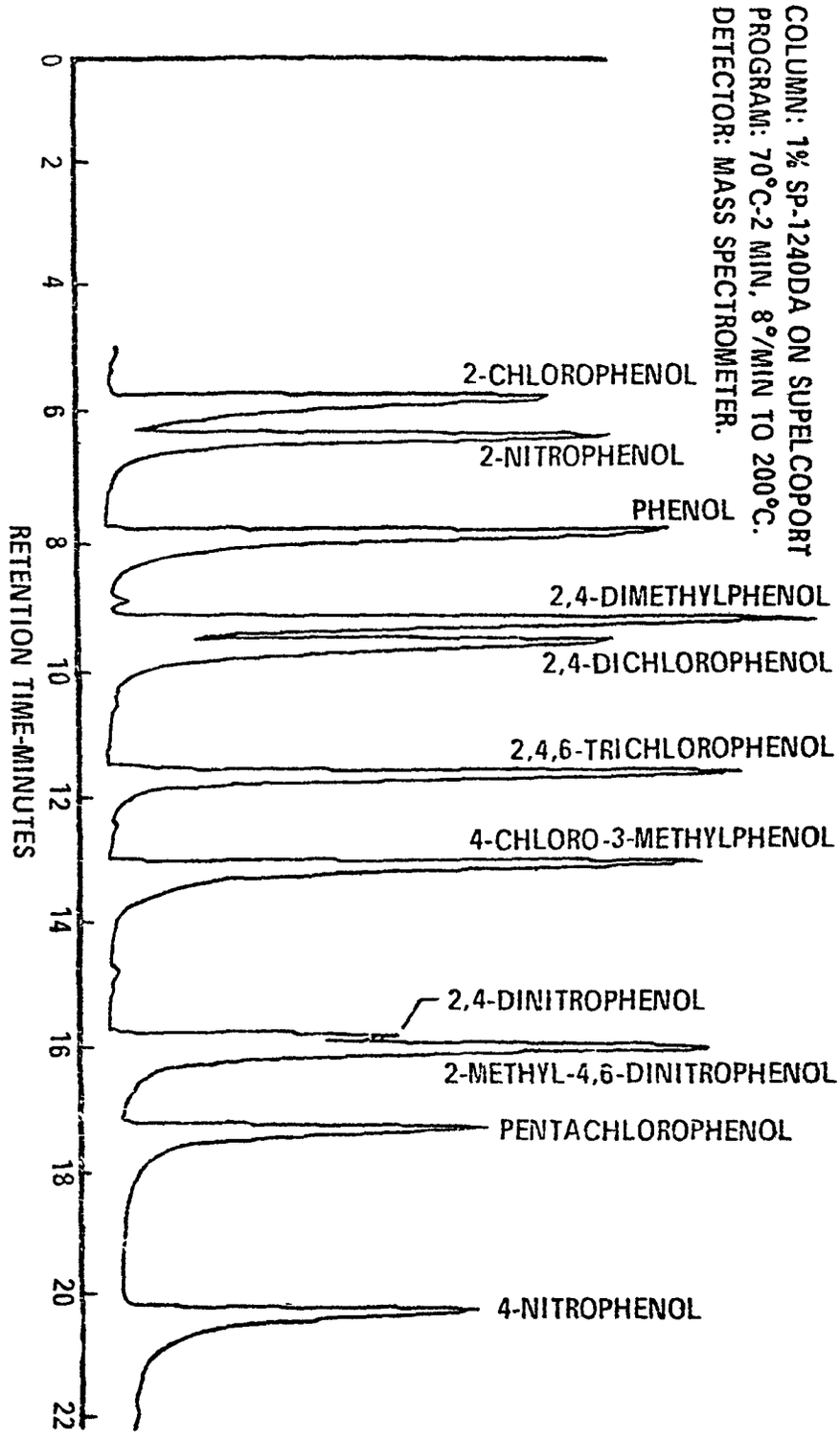


Figure 8.25-2
GAS CHROMATOGRAM OF ACID FRACTION

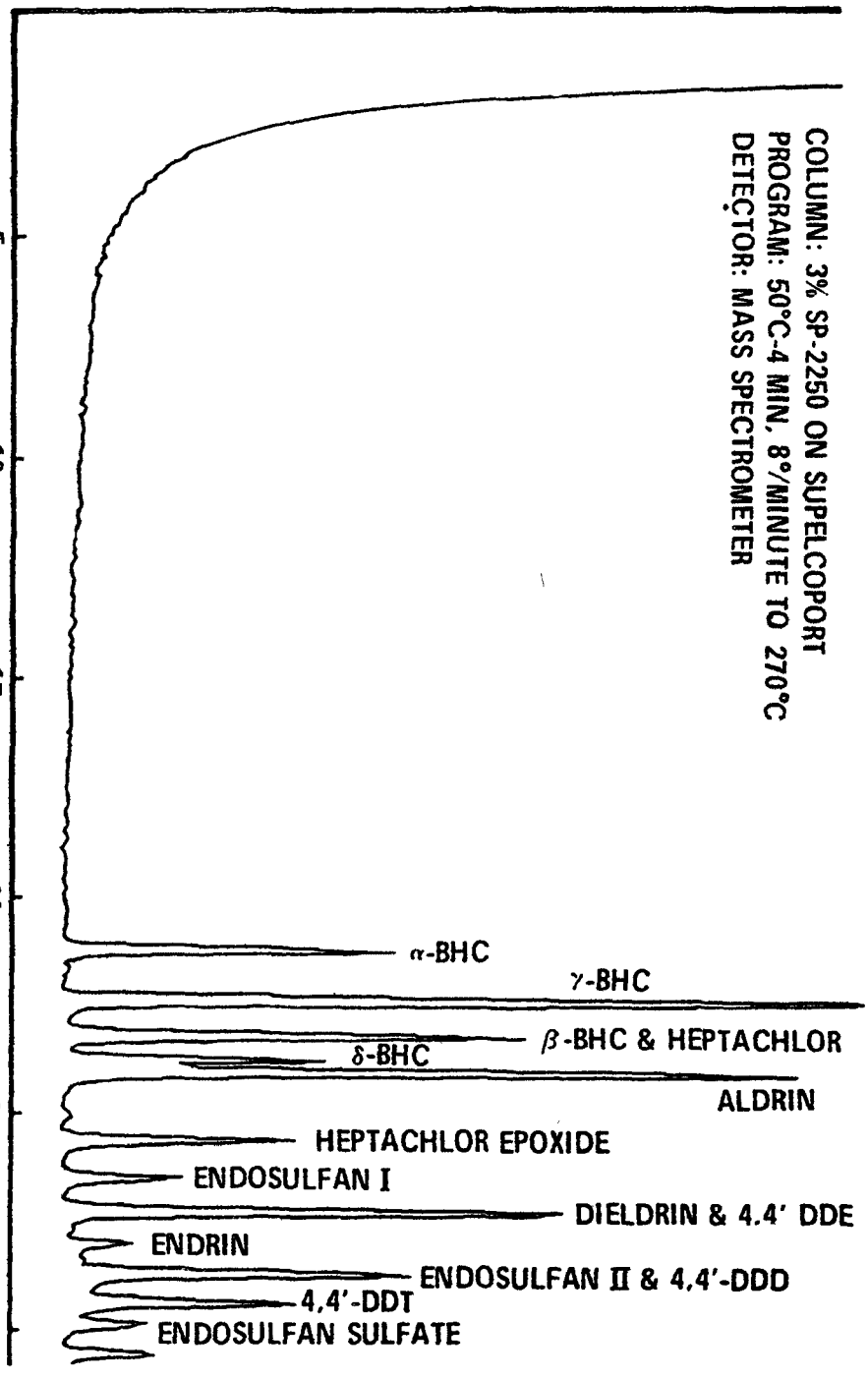


Figure 8.25-3
GAS CHROMATOGRAM OF PESTICIDE FRACTION

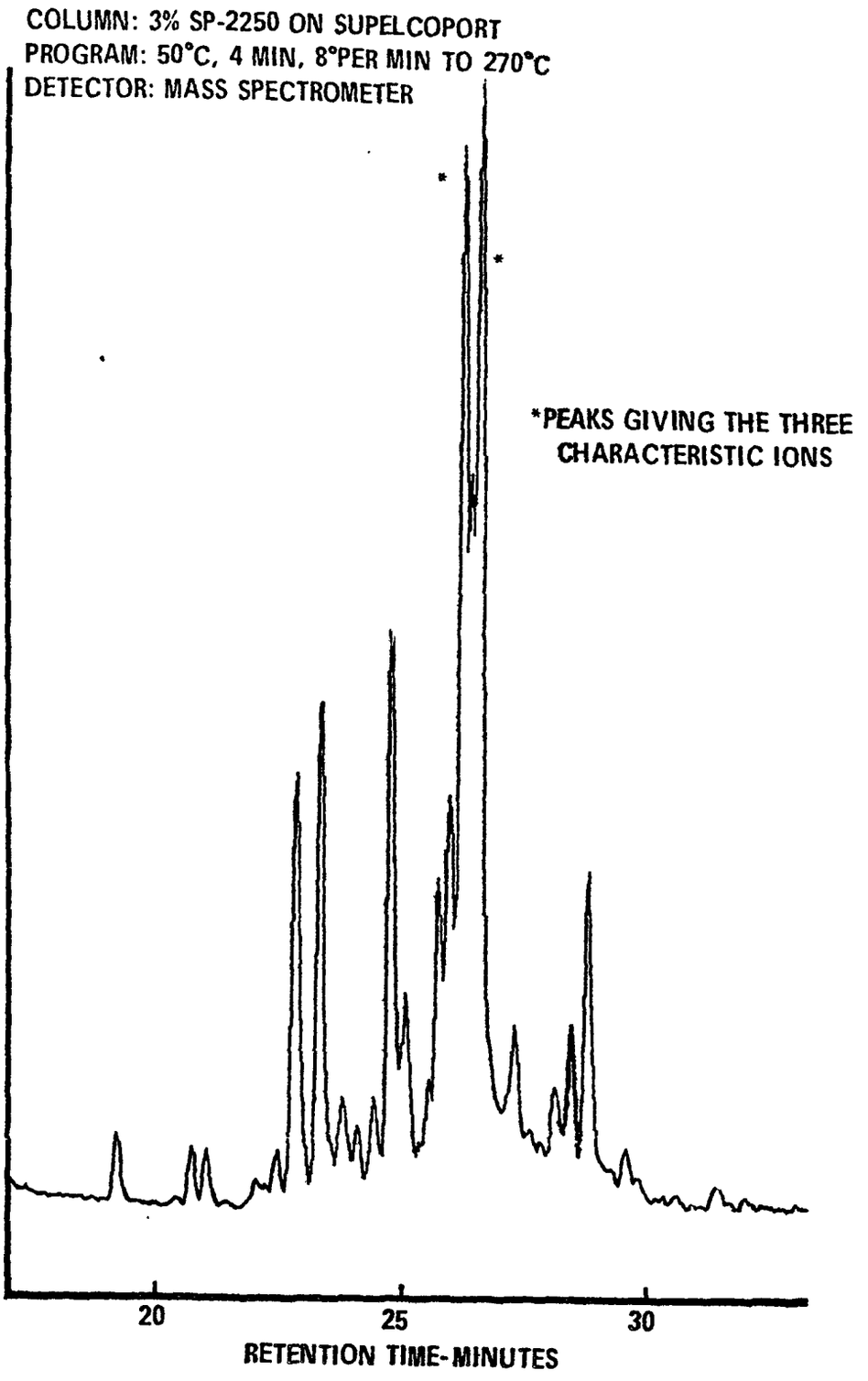


Figure 8.25-4
GAS CHROMATOGRAM OF CHLORDANE

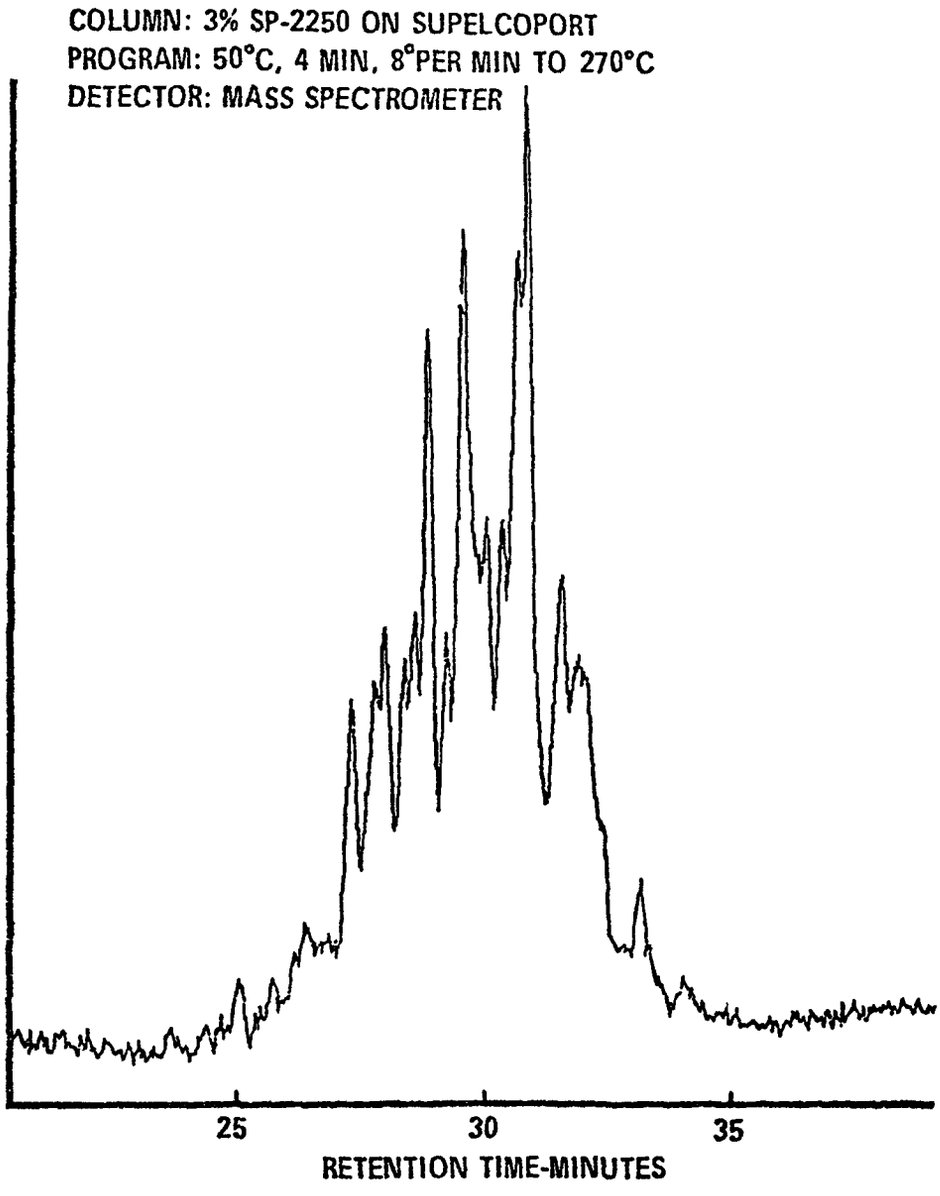


Figure 8.25-5
GAS CHROMATOGRAM OF TOXAPHENE

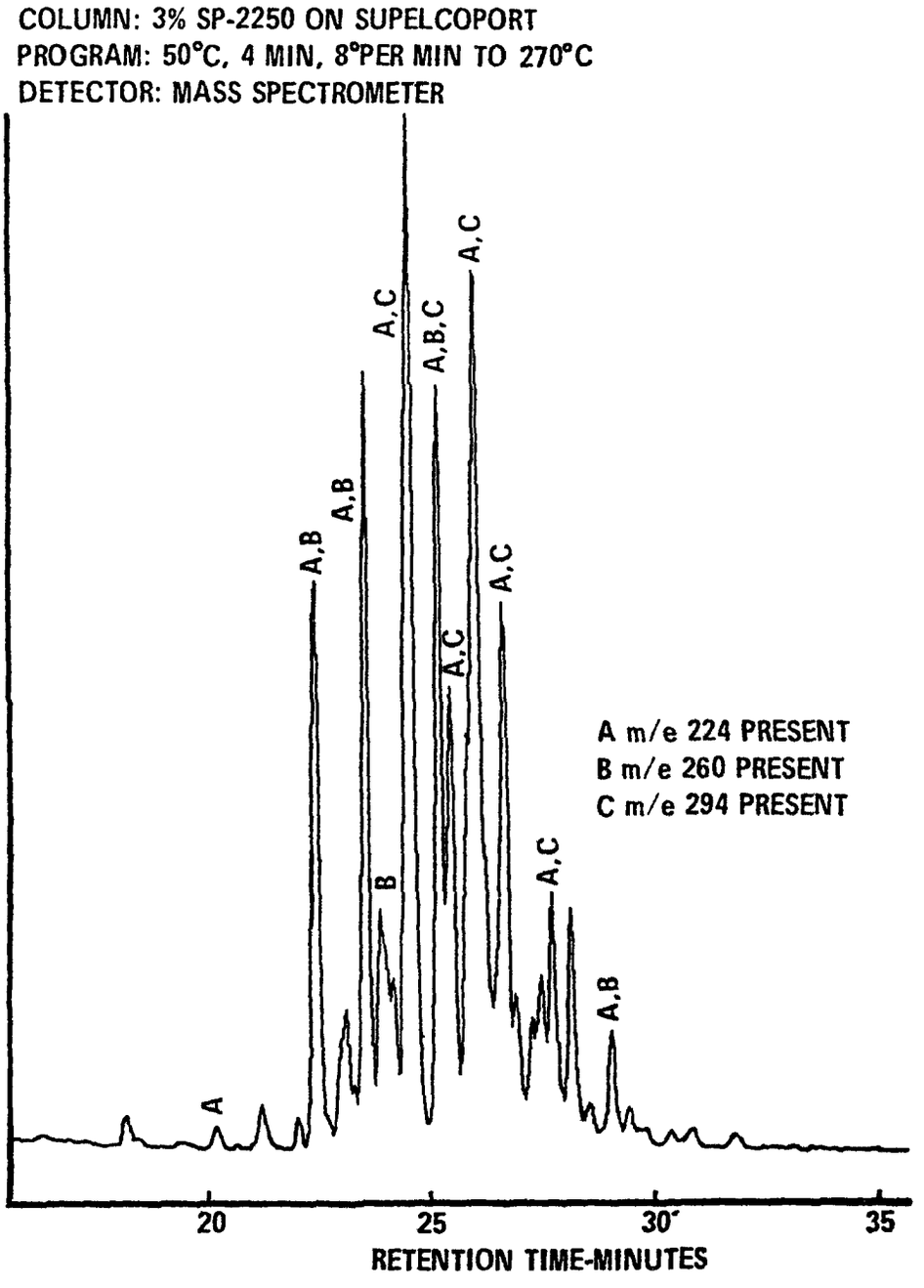


Figure 8.25-6
GAS CHROMATOGRAM OF AROCHLOR 1248

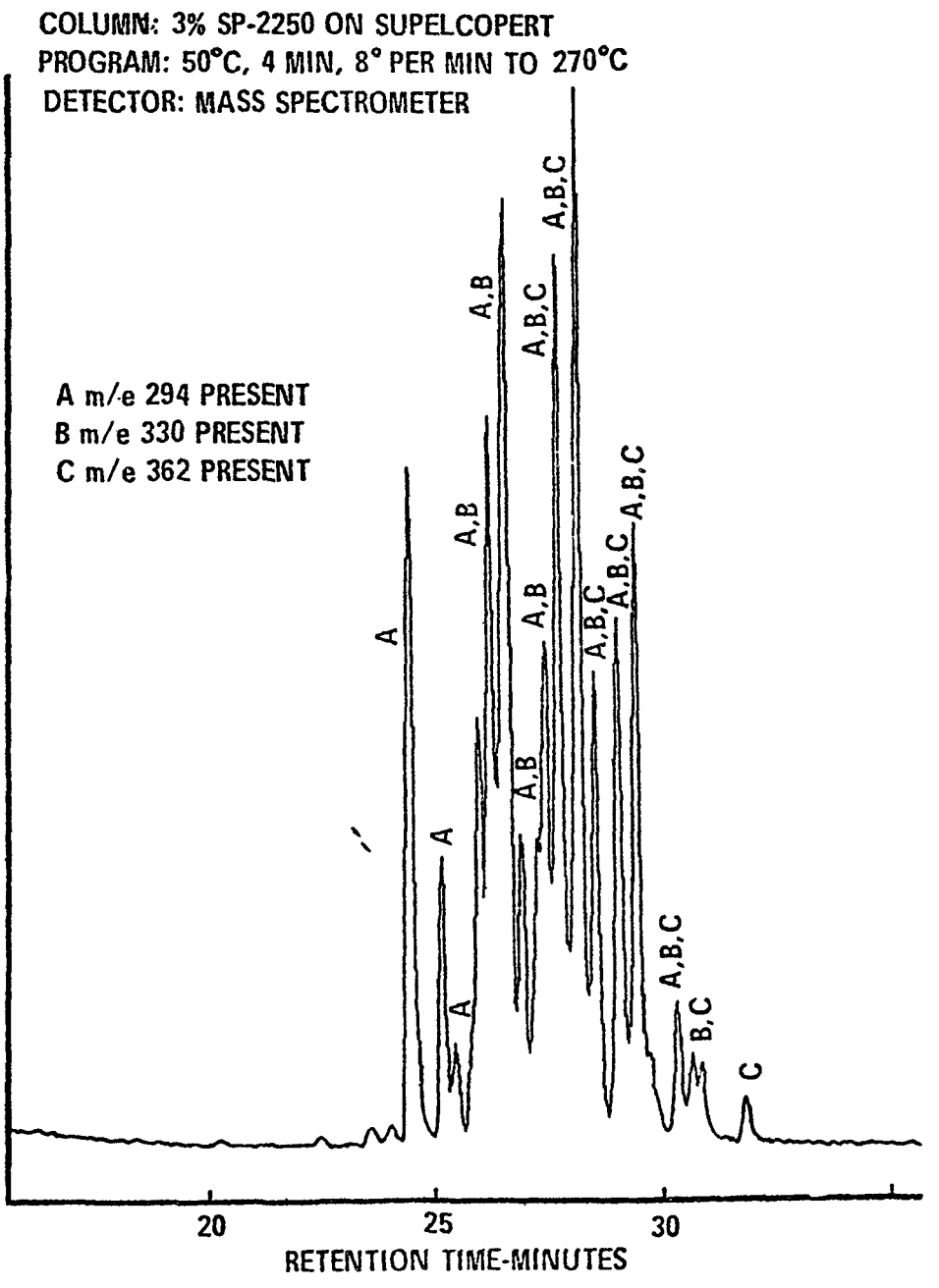


Figure 8.25-7
GAS CHROMATOGRAM OF AROCHLOR 1254

Method 8.49

GENERAL REQUIREMENTS FOR METALS ANALYSIS

1. It is essential to prevent contamination of the sample. Reagents must be of the highest grade and all laboratory equipment must be kept scrupulously clean and protected. Pipets with disposable tips are recommended. Glassware, plastic containers, and sample tubes should be subjected to the following series of washes in the order given:
   a. Thoroughly scrub with detergent and water.
   b. Rinse with a solution of one part concentrated nitric acid to one part water.
   c. Rinse with water.
   d. Rinse with a solution of one part hydrochloric acid and one part water.
   e. Rinse with water.
   f. Rinse with deionized distilled water.
   g. Dry the plastics at 50° C, the glassware at 105° C.
2. Sample bottles may be of borosilicate glass, polyethylene, polypropylene or teflon. It is recommended that they be used one time and discarded. If this is not feasible, they must be subjected to the series of washes listed in 1.
3. Deionized distilled water is made by passing distilled water through a mixed bed ion exchange resin column. All reagents, standards and dilutions shall be prepared using this water.

Method 8.27

Capillary Column GC/MS method for the analysis of Wastes

Scope and Application

This method may be used to determine the presence and concentration of the volatile and extractable organic compounds which are listed in Appendix VIII, 40 CFR 261.33 in wastes. The method employs capillary column gas chromatography-mass spectrometry. Quantitation can be performed in two ways depending on the level of information required.

Summary of Method

The waste is categorized by its physical makeup into one of the following three classes.

- Liquid (either single or multi-phase systems)
- Solid
- Combination of Liquid and Solid

Liquids are analyzed in their "as received" form except that if more than one phase is present the organic and aqueous phases are separated and the two phases analyzed separately. The organic phases are analyzed by direct injection onto the capillary column using either the split or splitless technique. Aqueous phases are determined by a combination of the purge and trap technique for volitiles and a series of extractions for the base/neutrals and acids. The extracted fractions are then combined and analyzed as a single solution using the splitless technique.

Solids are analyzed using purge and trap technique for volatiles and a soxhlet extraction for the extractables.

Samples containing both liquid and solid phases are first separated into their component liquid and solid phases using centrifugation. The separated phases are then analyzed as either liquids or solids as described above.

The components of the sample are quantitated in either of two ways, depending on the degree of quantitation necessary. The first way estimates concentration and assigns these estimated concentrations into ranges. Since this is not a rigorous quantitative procedure it may only be used for order of magnitude type estimates of concentration. These ranges are:

- Greater than 50%
- Between 10 and 50%
- Between 1 and 10%
- Between 100 ppm and 1%
- Between 1 and 100 ppm

For determining the precise concentration of a component in a sample the method of standard additions is employed.

Procedure

The analyst must first determine which category the sample belongs to.

- If the sample is a liquid go to the section labled "Liquids" (I) of this procedure.
- If the sample is a solid go to the section labled "Solids" (II) of this procedure.
- If the sample contains both liquid and solid go to the section labled "Mixtures of Liquids and Solids" (III) of this procedure.

I. Liquids

The analyst should determine if more than one liquid phase is present in the sample. If more than one phase is present the sample should be separated into its organic and aqueous phases respectively. This separation can be achieved by using either gravity or cenrifugation. The separated phases should be weighed. 10.0 gm of well mixed sample should be used.

A. Organic Liquids

1. Summary

Organic Liquids are injected directly onto the capillary column using either the split or splitless mode. The liquid may be diluted if necessary to facilitate sample handling or to accomodate the linear range of the mass spectrometer.

2. Apparatus and Materials

a. Sample Vials - 10 dram vials with teflon lined caps
b. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
c. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
d. Mass Spectrometer - Capable of scanning from 35 to 450 daltons every 1 second or less. The mass-spectrometer must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of DFTPP when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through either an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by placing the end of

the column in the ion source.

e. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored either within the data system or on line mass storage devices such as disk or tape. The system must have software available capable of searching GC/MS runs for the following:

   1) selected ion chromatograms
   2) total ion chromatograms
   3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base.

3. Reagents
   a. Methylene chloride - Pesticide quality
   b. Ethyl Ether - " "
   c. Ethylacetate - " "
   d. Methanol - " "
   e. Standards - Standards can be made up as necessary if appropriate reagents are available. Naphthalene-d_8 or phenanthrene-d_{10} may be used as internal standards.

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. The mass spectrometer should be scaned from 35 to 450 daltons in 2 sec or less. 50ng or less of DFTPP should be injected in the splitless mode using the conditions given in Table 8.27-1.
   b. The DFTPP spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in Table 8.24-2.

5. Sample Preparation
   a. If the liquid can be convieniently drawn into a 10 ul syringe, then no sample preparation is necessary. Weigh 1 gm of the liquid into a a pre-tared 10 dram vial. Add the internal standard at a level that would give 50 ng on column when injected. (The amount added will vary with split ratio)
   b. If it is necessary to dilute the sample, a weighed portion of the organic phase should be transfered to an appropriate volumetric flask and diluted to volume with one of the solvents listed in the reagent section. The internal standard is added at a level that would give 50 ng on column when injected prior to dilution. Record the dilution volume.

6. Gas Chromatography/Mass spectrometry
   a. Establish the chromatographic conditions given in table 8.27-1.
   b. Set the Gas Chromatograph for either split or splitless injection depending on estimated concentration. For example, an organic liquid that can be conveniently drawn up in a syringe can be analyzed using the split mode. An oily sample that needs to be diluted to 1:100 might best be handled using the splitless mode. If using the split mode, record the split ratio. Record both linear and volume column flow.
   c. Inject sample, start the chromatographic program, and acquire data. Record amount of sample injected. (1 to 5 ul when using split mode and 1 to 2 ul when the splitless mode is employed).
   d. Inject appropriate standards and acquire data using sample conditions as employed in c.

7. Qualitative and Quantitative Determination
   a. A compound will be judged to have been identified if either three or more characteristic ions of the compound maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yields a numerical value equivalent to the criteria stated above.
   b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and must be used when the actual concentration is needed. The second method is used when order of magnitude estimates of concentration are needed. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts, this condition should be met in the sample +20%
   c. Example Calculation
      5 ul of a 5 mg/ml solution of benzene was injected with a split ratio of 100:1 to produce the

chromatogram in figure 8.27-1. The integrated area of the benzene peak from the total ion chromatogram was 7840 counts. 10 gm of an organic liquid sample was disolved in methylene chloride in a volumetric flask to a final volume of 100 ml. 5 ul of this solution was injected with the same split ratio to produce the chromatogram in figure 8.27-2. The integrated area for benzene in this sample was 4235 counts. The peak for toluene gave an area of 4827 counts. The estimated concentration of benzene and toluene in this sample are:

Benzene Standard

5 mg/ml = 5 ug/ul

5 ug/ul x 5 ul = 25 ug injected

7840 counts/25 ug = 313.6 counts/ug

Benzene in Sample

4235 counts/5 ul injected x 1 ug/ 313.6 counts =

13.5 ug/5 ul

13.5 ug/5 ul x 1000 ul/ml =

2700 ug/ml

2700 ug/ml x 100 ml/10 gm dilution = 27000 ug/gm

27000 ug/gm = 27 mg/gm

27 mg/gm x 1 gm/1000 mg = .027 = 2.7%

The sample is 2.7% benzene

Toluene in sample

By an analogus method the sample is calculated to

be 3.1% toluene.

8. Report
   a. Report the results of each analysis giving the method used to quantify each comound. Report the scan number of each compound.
   b. Example:

Compound	Quantitation Method	Scan #	Amount	Range
Benzene	Estimate/Benzene	500	2%	1-10%
Toluene	Estimate/Benzene	622	3%	1-10%

B. Aqueous Liquid

1. Summary
   Aqueous liquids are analyzed by purge and trap and extraction methods given in Methods 8.83 and 8.84. After the aqueous sample is purged and traped and extracted by Methods 8.83 and 8.84 the traped material and the extracts (which have been combined) are analyzed by capillary column gas chromatography-mass spectrometry.

2. Apparatus and Materials
   See the appropriate sections in Methods 8.83, 8.84, and the apparatus and materials section for organic liquids in this method

3. Reagents
   See the appropriate sections in Methods 8.83, 8.84, and the reagents section for organic liquids in this method.

4. Calibration
   a. The mass spectrometer is calibrated with PFK or FC-43 over the scan range of interest. For the volatiles scan over the range 20 to 260 daltons, and scan over the range 35 to 450 daltons for the base/neutrals and acid extractables. The scan rates should be 2 sec. or less. 50 ng or less of bromoflurobenzene or DFTPP should be injected for the volitiles and extractables respectively. Chromatographic conditions are given in Tables 8.27-2 and 8.27-3.
   b. The specta obtained from the top of the chromatographic peak (background subtracted) should meet the criteia listed in Tables 8.24-2 and 8.24-3.

5. Sample Preparation
   a. Follow the purge and trap and extraction methods given in Methods 8.83 and 8.84 of this manual for preparation of the sample.
   b. Base/neutral and acid extractable fractions may be combined and analyzed in a single GC/MS analysis.

6. Gas Chromatography/Mass Spectrometry
   a. Establish the chromatographic conditions described in Tables 8.27-2 or 8.27-3, whichever is appropriate.
   b. Set gas chromatograph in either the split or

splitless mode. If using the split mode record the split ratio. Record both the linear and volume column flow.

c. When analyzing volatiles it may be necessary to adjust desorption time or cool the first few cm of the column with a flurocarbon spray in order to maintain chromatographic resolution.

d. Inject sample and acquire data, recording the amount injected. Follow the same procedure for any standards.

7. Quantitative and Qualitative Determination

a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within ± 20%; or, a reverse search yeilds a numerical value equivalent to the criteria stated above.

b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentartion. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts, this condition should be met in the sample ±20%

c. Example Calculation

A 10 gm sample contained 3.5 gm of organic liquid with a volume of 3.9 ml. 5 ul of the organic liquid was injected with a split ratio of 100 to 1. The integrated area of benzene gave 3582 counts. Benzene in the organic phase is calculated:

3582 counts/5 ul x 1 ug/313.6 counts = 11.4 ug/5 ul

11.4 ug/5 ul x 1000 ul/ml = 2280 ug/ml

the density is 3.5gm/3.9ml = .9 gm/ml

2280 ug/ml = 2.28mg/ml

2.28mg/ml x 1gm/1000mg x 1 ml/.9gm = .0025 = .25%

The purge and trap analysis of the aqueous phase was performed on 6.5 gm of liquid. Benzene gave 12562 counts. The benzene in the aqueous phase is:

12562 counts/6.5 gm x 1 ug/313.6 counts =

40.0 ug/6.5 gm = 6.2 ppm

This is insignificant compared to .25%

The total amount of benzene in the sample is calculated:

.25% x .35 of total = .0875% or 875 ppm

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

Compound	Quantitation Method	Scan #	Amount	Range
Benzene	Estimate/Benzene	687	875ppm	100ppm-1%

II. Solids

Two samples of well mixed solid should be used in this analysis. One sample is used for the purge and trap analysis of volatiles and one for soxhlet extraction analysis.

A. Purge and Trap Determination of Volatiles in Solids

1. Summary
An appropriate weight of sample (1-10 gm) is diluted with 10 ml of organic-free water. The diluted sample is purged for 12 min. with inert gas at room temperature. The gaseous phase is passed through a sorbent trap where the organic compounds are concentrated. The contents of the trap are desorbed into the GC/MS by heating and backflushing the trap.

2. Apparatus and Materials
   a. See the apparatus section of Method 8.83 of this manual.
   b. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
   c. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
   d. Mass Spectrometer - Capable of scanning from 20 to 260 daltons every 1 second or less. The MS must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of BFB when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by directly connecting the end of the column to the ion source.
   e. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored either within the data system or on line mass storage devices such as disk or tape. The system must have software available capable of searching GC/MS runs for the following:

      1) selected ion chromatograms
      2) total ion chromatograms

3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base

3. Reagents - Standards as necessary (See Methods 8.24, 8.83, and I-A-3e of this Method)

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. 50ng or less of BFB should be injected in the splitless mode using the conditions given in table 8.27-3.
   b. The spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in table 8.24-2.

5. Sample Preparation
   a. Weigh an appropriate sample into a pretared 10 to 15 ml Teflon lined, screw-capped vial.
   b. Dilute the sample with 10 ml distilled water. Disperse the sample into the water. Transfer the total sample to the purging device using a syringe with an 1/8 in. gauge Teflon needle. Seal the sample in the purging device. Add the internal standard and purge with 40 ml/min (He or N_2) for 12 min. at room temperature.

6. Gas Chromatography/Mass spectrometry
   a. Establish the chromatographic conditions given in table 8.27-1.
   b. Set up the Gas Chromatograph for either split or splitless injection. If using the split mode, record the split ratio, linear and volume column flow.
   c. The first few inches of the column should be cooled using flurocarbon spray. Heat the trap to 200°C. Backflush it for 4 min in the desorb mode into the gas chromatograph.

7. Qualitative and Quantitative Determination
   a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yeilds a value equivalent to the criteria stated above.
   b. Samples can be quantitated in two ways. The first is by the method of standard additions. This

method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentration as given on page 1 of this method. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts this condition should be met in the sample $\pm$20%.

c. Example Calculation

5.0 gm of a solid sample was mixed with 10 ml water and purged and traped by the procedure specified. A splitless injection gave 29,043 integrated area counts for toluene. 1 ul of a standard solution of Toluene 100 ug/ml gave 16,290 integrated counts.

16290 counts/ 1 ul x 1000 ul/100 ug = 162900 counts/ug

29043 counts/5 gm x 1 ug/162900 counts = .18 ug/5 gm

.18 ug/5 gm = .036 ug/gm = .036 ppm

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

      The level of toluene in the sample is very low and for the purpose of this analysis is reported at less than 1 ppm

B. Soxhlet Extraction for Solids

1. Summary
The sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool and extracted using methylene chloride. The extract is reserved. The remaining contents of the thimble are mixed with distilled water and the pH is adjusted to 2 or less. This aqueous mixture is extracted with ethyl ether. The two extracts are dried, combined, and anaylzed in one GC/MS analysis.

2. Apparatus and Materials
   a. Soxhlet extractor - 40 mm id, with 500 ml round-bottom flask.
   b. Kuderna-Danish Apparatus [Kontes K-570000 or equivalent] with 3-ball snyder column
   c. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
   d. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
   e. Mass Spectrometer - Capable of scanning from 35 to 450 daltons every 1 second or less. The MS must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of DFTPP when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by directly connecting the end of the column to the ion source.
   f. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored within the data system. Mass storage devices such as disk or tape are accepable. The system must have software available to allow searching GC/MS runs for the following:
      1) selected ion chromatograms
      2) total ion chromatograms
      3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base

3. Reagents
   a. Methylene chloride - Pesticide grade
   b. Ethyl Ether - Pesticide grade

c. Anhydrous Sodium Sulfate, ACS grade, purified by heating at 400°C for 4 hr. in a shallow tray.

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. 50ng or less of DFTPP should be injected in the splitless mode using the conditions given in table 8.27-1.
   b. The DFTPP spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in table 8.24-2.

5. Sample Preparation
   a. Blend 10.0 gm of the solid sample with 10.0 gm of anhydrous sodium sulfate. Weigh this mixture to the nearest 0.1 gm. Place in either a paper (pre-washed with methylene chloride and dried) or glass extraction thimble.
   b. Place the thimble in the extractor. (If any problems arise when using the thimble, i.e. if the sample clogs the thimble, an alternative would be to place a plug of glass wool in the extraction chamber, transfer the sample into the chamber, then cover the sample with another plug of glass wool.)
   c. Place 250 ml of methylene chloride into the 500 ml roundbottom flask, add a boiling chip and attach the flask to the extractor. Extract the sample for 16 hours.
   d. After the extraction is complete, cool the extract; rinse extractor flask and thimble with fresh solvent. Combine the extract and rinse. Dry the extract by passing it through a 4 inch column of sodium sulfate that has been washed with solvent. Collect the dried extract in a 500 ml Kuderna-Danish (KD) flask fitted with a 10 ml graduated concentartor tube. Empty the contents of the thimble into a pre-weighed 250 ml Erlinmeyer flask. Add 100 ml distilled water to the flask.
   e. Adjust the pH to 2 or less with sulfuric acid solution. Extract three times with fresh 60 ml portions of ethyl ether. Combine the three extracts and dry by passing through a 4 inch column of sodium sulfate. Rinse column with fresh solvent. The dried extract is added to the KD.
   f. Evaporate the aqueous solution in the erlinmeyer flask to dryness; cool the flask and weigh the residue. Determine the weight difference between

the residue in the erlinmeyer flask and the original sample.

g. Concentrate the dried extracts in the KD. A level that would give a final concentration of about 1 mg/ml is generally appropriate for GC/MS.

h. The concentrated extract should be placed in a volumetric flask and made up to the appropriate volume.

6. Gas Chromatography/Mass spectrometry

a. Establish the chromatographic conditions given in table 8.27-1.

b. Set the Gas Chromatograph for either split or splitless injection. If using the split mode, record the split ratio. Record both liniar and volume column flow.

c. Inject sample and acquire data. Record amount of sample injected. (2 to 5 ul for split and 1 to 2ul for splitless)

d. Inject appropriate standards and acquire data as in c.

7. Qualitative and Quantitative Determination

a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yeilds a value equivalent to the criteria stated above.

b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentartion. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts this condition should be met in the sample $\pm$20%.

c. Example Calculation
10 gm of solid sample was extracted with methylene chloride and ethyl ether as in the procedure. The

sample lost about 4 gm during the extraction. The combined extracts were diluted to 500 ml with methylene chloride. 5 ul was injected with a split ratio of 100 to 1. Hexachlorobenzene was found in the extract with a total of 7,121 total area counts.

Dichlorobenzene was used as a standard

5 ul x 1 mg/ml x 1 ml/1000 ul = 5 ug

Total counts for Dichlorobenzene was 3760

3760 counts/5 ug = 752 counts/ug

Hexachlorobenzene in sample

7121 counts/5 ul x 1 ug/752 counts = 9.47 ug/5 ul

9.47 ug/5 ul x 1000 ul/1 ml x 500 ml = 947000ug

947000 ug = .947 gm

.947 gm/10 gm = .0947 = 9.5% hexachlorobenzene

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

Compound	Quantitation Method	Scan #	Amount	Range
Hexachloro benzene	Estimate/dichloro benzene	693	9.5 %	1-10%

III. Mixtures of Liquids and Solids

A 10 to 20 gm sample of well mixed waste is used. The sample is divided into its component phases and the procedures oulined in sections I and II of this Method are employed for analysis.

A. Separation Procedure for Liquids and Solids

1. Summary
   A 10 to 20 gm sample of the waste is separated into its component phases by centrifugation. The Liquid Phases are either decanted or pipeted for analysis using section I and the solid residue is analyzed using section II.

2. Apparatus and Materials
   a. Centrifuge tubes - 10-20 ml pyrex glass or equivalent with ground glass stopper.
   b. Centrifuge - Capable of 2400 RPM

3. Reagents - Reserved

4. Calibration - See calibration sections in parts I and II of this method

5. Sample Preparation
   a. Alliquot a 10 to 20 gm sample of well mixed waste into a pre weighed cenrifuge tube. Weigh.
   b. Place tube into centrifuge and spin at 2400 RPM for 15 min. or until the solids and liquid phases are separated.
   c. Pour off liquid phase and weigh. Proceed to section I of this method.
   d. Weigh remaining solids and proceed to section II of this method. The purge and trap method for the determination of volatiles in solids may be omitted since the volatiles are determined in the liquid phase of the sample.

B. Report

1. Report the results as a weighted average of the liquid phases and solid phase.
2. Example calculation
   See sections I and II

Table 8.27-1 (Liquids)

Column: SE-30, SE-52, SE-54 (30 m)
Linear Flow Rate: 50 cm/sec H_2 or 30 cm/sec He
Temperature Program: Inject at 25°C then 50°C
Program 50° to 280° C at 8°/min
Hold at 280°C for 15 min.

Table 8.27-2 (Extractables)

Column: SE-30, SE-52, SE-54 (30 m)
Linear Flow Rate: 50 cm/sec H_2 or 30 cm/sec He
Temperature Program: Inject at 50°C hold 2 min.
Program to 280°C at 8°C/min
Hold at 280°C for 15 min

Table 8.27-3 (Volatiles)

Column: Same as 8.27-2
Linear Flow Rate: Same as 8.27-2
Temperature Program: Inject at 25°C (cool head of column with flurocarbon spray) then to 50°C
Program 50°C to 200°C at 4°C/mir
Hold at 200°C for 10 min

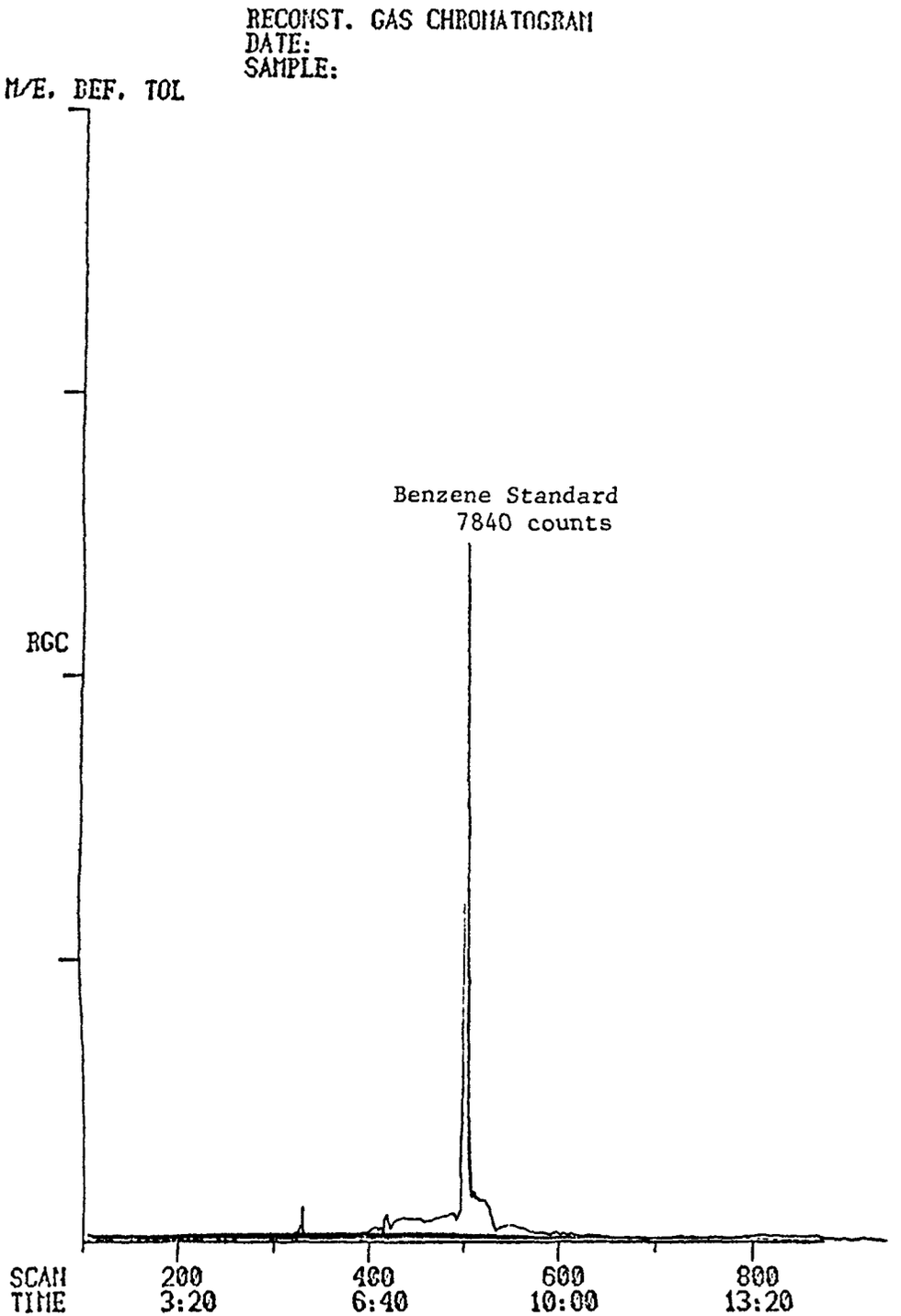

RECONST. GAS CHROMATOGRAM
DATE:
SAMPLE:
M/E. BEF. TOL
Benzene Standard
7840 counts
RGC
SCAN
TIME
200
3:20
400
6:40
600
10:00
800
13:20

Figure 8.27-1

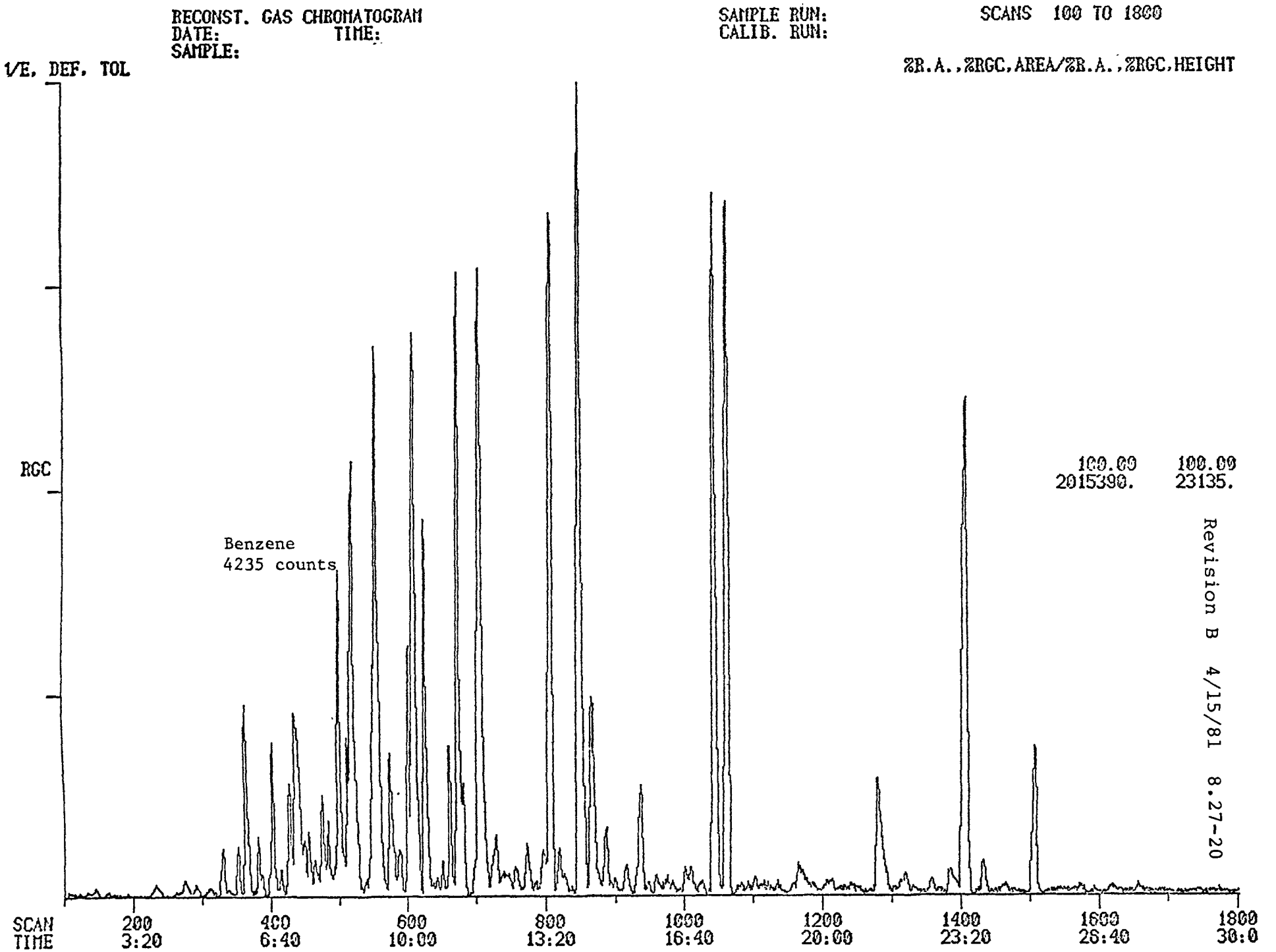

RECONST. GAS CHROMATOGRAM
DATE: TIME:
SAMPLE:
SAMPLE RUN:
CALIB. RUN:
SCANS 100 TO 1800
1/E, DEF, TOL
%R.A.,%RGC,AREA/%R.A.,%RGC,HEIGHT
RGC
100.00 100.00
2015390. 23135.
Benzene
4235 counts
Revision B 4/15/81 8.27-20
SCAN 200 400 600 800 1000 1200 1400 1600 1800
TIME 3:20 6:40 10:00 13:20 16:40 20:00 23:20 26:40 30:0

Figure 8.27-2

4. Acids must be Spectrograde. If metals are found to be present the acid they should be diluted 1:1 with distilled water and redistilled in a hood.
5. An Atomic Absorption Spectrophotometer provides the simplest and most accurate means of determining metal concentrations in the low ranges required. In principle, a prepared solution is vaporized in a flame. Metal atoms in the flame are capable of absorbing light of a particular and characteristic wavelength. When a light beam, which emanates from the pure metal in a cathode lamp, is passed through a flame, the absorption is proportional to the concentration. Through various detecting devices, this absorption may be read directly or be recorded as a peak on a strip chart recorder.

   Most metals may be determined in an air plus acetylene flame. However, some metals require more energy in order to dissociate and a nitrous oxide - acetylene flame must be used. Additionally, when the fuel itself absorbs a particular wavelength, then the fuel may be changed to a non-interfering one.

   The most common type of burner is known as a "premix" in which the spray is mixed with air or oxidant. It may be fitted with a conventional head (4 inch single slot), a 3 slot "Boling" head for air-acetylene fuel, or a 2 inch short slot for use with nitrous oxide-acetylene fuel. These various heads influence the burning rate, carbon build-up and sensitivity. The instrument manual

will list the head that has been found to work best for a given element.

A graphite furnace is especially useful for measuring low levels. In this device the sample is evaporated in a graphite tube, charred and vaporized in a confined and inert atmosphere. However, this method is susceptible to interference from chlorides and other dissolved solids. If the samples smoke, light scattering can occur which causes erroneously high results. A deuterium background corrector should be employed to correct for non-specific interference.

The spectrophotometer chosen should have a wavelength range of 190 to 800 nanometers, and use an output device with high sensitivity and fast response time. The instrument may provide direct readout or use a 10 millivolt strip chart recorder. The use of a recorder will furnish a permanent record of the analysis and the operating conditions.

Single element hollow cathode lamps are preferred. Electrodeless discharge lamps may also be used when available.

Venting

A vent must be installed 6 to 12 inches above the burner to remove toxic fumes and vapors. The slight vacuum insures a constant air flow which tends to stabilize the flame. A variable speed blower is an advantage in that the air flow may be adjusted to prevent disturbance of the flame.

7. Instrument Operation

Procedures vary with the particular model and manufacturers' instructions should be followed. In general, the following should be carried out:

a. Install the selected cathode lamp.

b. Install the proper burner head.

c. Set the wavelength dial and align the lamp.

d. Set the slit width.

e. Turn on the instrument and apply correct current.

f. Allow the instrument to warm up. This time varies but is usually around 20 minutes.

g. Turn on the air and adjust flow rate.

h. Turn on the acetylene, adjust flow rate and ignite flame. Note that it may be necessary to reduce the fuel flow if the sample fluid acts as as a fuel.

i. Atomize deionized distilled water acidified with 1.5 ml concentrated nitric acid per liter, and check the aspiration rate. Adjust the rate to between 3 and 5 ml per minute. Zero the instrument.

j. Atomize a solution containing a known amount of test element and adjust the burner up, down or sideways to get maximum response.

k. When analyses are finished, turn off the acetylene first and then the air.

Optimum Concentration Range

The most accurate results may be obtained in this range

and it varies for different elements and for different instruments. It may be necessary to dilute a sample of higher concentration in order to keep it in this range, in which case the value obtained must be doubled, tripled, etc. accordingly.

In the case of lower concentrations it may be sufficient to show that the sample is below the required limit and therefore non-hazardous. When the generator wishes to know the exact level, it may be possible to concentrate a sample to bring it into the optimum range.

It is necessary to correct for background absorption for precise work. A double beam instrument or dual double beam system permits a wider range of selectivity and precision. A background corrector is frequently useful to minimize background absorption.

Calibration

The concentration of metal in the sample is determined by comparing its absorbance to that of solutions of known concentration. The samples are preserved at a pH of less than 2 with nitric acid, and calibration is performed with distilled deionized water acidified in the same way.

Quantification

When analyzing industrial wastes or the Toxicant Extraction Procedure extract, where unknown dissolved materials may interfere with the determination, the Method of Standard Additions must be used:

Method of Standard Additions

In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The final volume of the blank and of the standards must be the same so that the interfering substance is present in the same amount. The absorbance of each solution is determined and then plotted on the vertical axis of a graph with the concentrations of the standard plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown below:

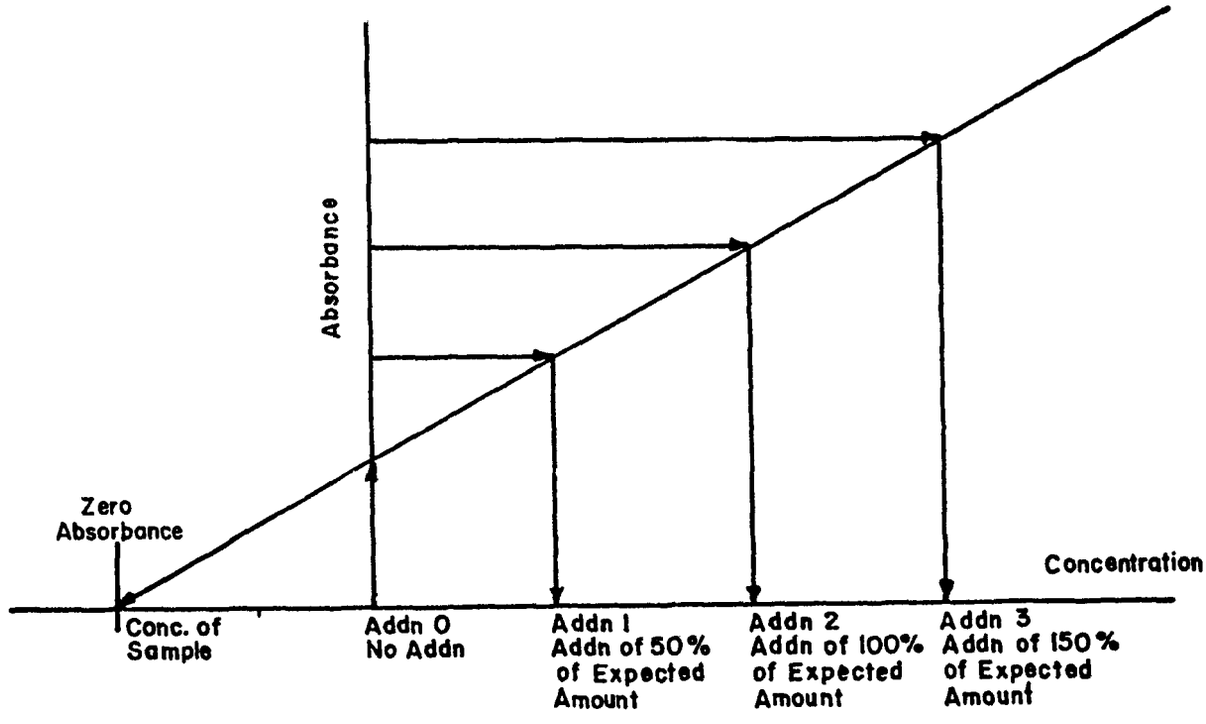


Figure 8.49-1
PLOT OF METHOD OF STANDARD ADDITIONS

Note: For this method to be valid, the plot must be linear. The slope of this line should not differ by more than 20% from the slope of the standard solutions. The effect of the assumed interference must not change as the proportion of sample to standard changes.

Solids, Sludges and Slurries

Solids, sludges and slurries may be analyzed by these methods by weighing out suitable portions and digesting as described for each metal. The material is then filtered through a 0.45 micron filter while washing down the sides of the beaker and rinsing the filter with distilled deionized water. The filtrate is then made up to a suitable volume and analyzed in the ususal manner. Results can be related back to the original sample weight and reported as mg/kg.

Conclusion

The details of the following approved methods are examples of acceptable techniques. Dilutions and concentrations may have to be varied to suit the instrument being used. It is important not to overwhelm the instrument with very high concentrations above the optimum recommended range. Contamination can result which is difficult to remove. At the same time, many dilutions introduce error which can be avoided by some knowledge of the waste beforehand. If nothing is known, caution is advised.

For additional information the applicable sections of "Methods for Chemical Analysis of Water and Wastes", EPA 600/4-79-020 (Appendix II of this manual) may be consulted.

Method 8.50

ANTIMONY

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of antimony in a waste or Extraction Procedure Extract

Summary of Method

A sample is digested using nitric acid and the concentration of antimony measured using either a flame or graphite furnace equipped atomic absorption spectrometer. The flame method is most accurate when employed with solutions containing 1 - 40 mg/liter antimony while the graphite furnace procedure is best suited for solutions containing 20 - 300 ug/liter.

Apparatus

Atomic absorption spectrometer equipped with either a graphite furnace or flame burner head as described in Section 8.49.

Reagents

1. When using the flame procedure air and acetylene are required. Air should be 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. High purity acetylene should be used. Acetone which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 7 kg/cm^2 (100 psig) acetylene.

2. Nitric Acid, J.T. Baker Ultrex Grade or equivalent.
3. Antimony potassuim tartrate, analytical reagent grade.
4. Hydrochloric Acid Solution, J.T. Baker Ultrex Grade or equivalent diluted 1:1 with distilled deionized water.

Procedure

Standard Solutions

1. Prepare Antimony Standard Stock Solution by dissolving 2.7426 g antimony potassium tartrate, analytical reagent grade, in distilled deionized water containing 1.5 ml HNO_3/liter and bringing to volume in a 1 liter volumetric flask (1 ml = 1 mg Sb).
2. Prepare working standards from stock solution. If it is desired to work in the optimum concentration range, using the flame technique, the following is suggested:
   a. Transfer 0, 0.1, 1.0, 2.0, 3.0, and 4.0 ml of stock solution to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 2 ml HNO_3/liter. The concentrations of these working standards are 0, 1, 10, 20, 30 and 40 mg Sb/liter.
3. When using the graphite furnace procedure working standards should be prepared to cover the range 20 to 300 ug Sb/liter by preparing dilutions of the above working standards.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, so that the sample does not boil. Cool, and add another 3 ml conc.

HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 1 ml of 1:1 HCl and warm the beaker in order to dissolve any precipitates. Cool the beaker. Transfer to a 100 ml volumetric flask and bring to volume using distilled deionized water containing 2 ml HNO_3/liter. Note that hydrochloric acid is used to aid in dissolving of antimony residues.

2. If particulates such as silicate remain in the sample, it must be centrifuged and the supernatant sampled.

Standard Addition

a. Take the 50, 75, and 100 ug standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water. This is the blank.

Note: The absorbance from the blank will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standard plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 217.6 nanometers
Note: The presence of lead in the waste may interfere since lead absorbs at this wavelength. In this case, use the 231.1 nanometer antimony line.

Optimum Concentration Range: 1-40 mg/liter

Lower Detectable limit: 0.2 mg/liter

Fuel: Acetylene

Oxidant: Air

Type of Flame: Lean

A general outline for instrument operation is given in Section 8.49. Follow the manufacturer's instructions for the Spectrophotometer being used.

Graphite Furnace Method

Wavelength: 217.6 nanometers

Optimum Concentration Range: 20-300 ug/liter

Lower Detection Limit: 3 ug/liter

Purge gas: Argon or nitrogen

Drying time and temperature: 30 sec at 215° C

Ashing time and temperature: 30 sec at 800° C

Atomizing time and temperature: 10 sec at 2700° C

The conditions listed above are based on a 20 ul injection; continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual. Note: If the chloride presents a matrix problem, add an excess of 5 mg ammonium nitrate to the furnace and ash using a ramp

accessory; or with incremental steps, until ashing temperature is reached.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as described in Section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line, a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.51

ARSENIC

Scope and Application

The following atomic absorption procedures are approved for determining the concentration of arsenic in a waste or Extraction Procedure Extract. Both methods are generally acceptable for RCRA type samples. However, the graphite furnace method is sensitive to the presence of chlorides and dissolved solids in the sample, while the hydride method requires greater preparation and is sensitive to high concentrations of chromuim, copper, mercury, silver, cobalt, and molybdenum.

Summary of Methods

In the furnace method the sample is digested using nitric acid and hydrogen peroxide. The method is most accurate for solutions containing 5 - 100 ug Arsenic/liter.

In the gaseous hydride method the sample is digested using nitric and sulfuric acids. The arsenic is then reduced to the trivalent form with stannous chloride, and converted to arsine, AsH_3, using zinc metal. The hydride is swept into an argon entrained hydrogen flame for analysis. It is most accurate when employed for solutions containing 2 - 20 ug As/liter. However, mercury, silver, cobalt and molybdenum can interfere in the analysis.

Preoxidation (digestion) is required in both methods in order to convert organic forms of arsenic to the inorganic form, and to remove organic interferences.

Precaution

Severe poisoning can result from ingestion of as little as 100 mg Arsenic. Chronic effects can appear with constant intake of lower levels. Exercise care in the handling and cleanup of the materials and work area.

Graphite Furnace Method

Apparatus

1. Atomic absorbtion spectrometer equipped with a non-pyrolytic graphite furnace.

Reagents

1. Standard Stock Solution

   Stock solution may be purchased, or prepared as follows:

   a. Dissolve 4g NaOH in 100 ml distilled deionized water. Dissolve 1.3203 g of analytical reagent grade arsenic trioxide (As_2O_3) in the solution.

   b. Acidify this solution with 20 ml concentrated HNO_3.

   c. Transfer to a 1 liter volumetric flask with careful rinsing, and bring to volume with distilled deionized water. The concentration of this solution is 1000 mg arsenic/liter (1 ml=1 mg As).

2. Nickel Nitrate Solution, 5%

   Dissolve 24.780 g of ACS Reagent Grade $Ni(NO_3)_2 \cdot 6H_2O$ in distilled deionized water and make up to 100 ml.

3. Nickel Nitrate Solution, 1%

   Dilute 20 ml of the 5% solution to 100 ml with distilled deionized water.

4. 30% Hydrogen Peroxide, ACS Reagent Grade
5. Sodium Hydroxide, ACS Reagent Grade
6. Concentrated Nitric Acid, J.T. Baker Chemical Co. Ultrex Grade or equivalent.

Procedure

1. Transfer 100 gm (or in the case of EP Extract analysis 100 ml) of well mixed sample to a 250 ml beaker and add 2 ml of 30% H_2O_2 and 1 ml of concentrated HNO_3. Heat on a hot plate for 1 hour at 95°C or until the volume is less than 50 ml. It may be necessary to repeat this operation to digest all of the material present.
2. Cool, transfer to 50 ml volumetric flask and bring to volume with distilled deionized water.
3. If particulate matter remains, after oxidation, it must be removed by centrifugation and only the supernatant used.
4. Pipet 25 ml of this solution into a 50 ml volumetric flask. Add 5 ml of 1% nickel nitrate solution and bring to 50 ml with distilled deionized water. The sample is ready for injection.
5. Prepare standards from stock solution. The following provides standards covering the optimium working range:
6. Pipet 1 ml stock solution into a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml conc. HNO_3 per liter. The concentration of this solution is 1 mg As/liter (1 ml=1 ug As).
7. Prepare 6 working standards by transferring 0, 1.0.

2.5, 5, 7.5, and 10 ml from (a) into 100 ml volumetric flasks. Add to each flask 1 ml concentrated HNO_3, 2 ml 30% H_2O_2 and 2 ml 5% nickel nitrate solution, bring to volume with distilled deionized water. The concentrations of these working standards are 0, 25, 50, 75, and 100 ug As/liter. They are ready for injection.

8. Take the 50, 75, and 100 ug/liter standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Add 0.3 ml of 1% of nickel nitrate solution, and 0.3 ml H_2O_2 solution. Bring to volume with distilled deionized water.
9. Add 2 ml of prepared sample to a 10 ml volumetric flask. Add 0.8 ml nickel nitrate solution and 0.8 ml H_2O_2 solution. Bring to volume with distilled deionized water. This is the blank.

Note: The absorbance from the blank, will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimium absorbance can be judged.

Instrument Operation:

Wavelength: 193.7 nanometer

Optimum Concentration Range: 5-100 ug/liter

Lower Detection Limit: 1 ug/liter

Drying time and temperature: 30 sec at 125°C

Ashing time and temperature: 30 sec at 1100°C

Atomizing time and temperature: 10 sec at 2700°C

Purge gas: Argon

These conditions are based on a 20 ul injection; continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer Model HGA 2100 furnace. Other equipment will have different operating requirements. For specific information, the manufacturer of the instrument should be consulted.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as described in Section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Gaseous Hydride Method

Reagents

1. Potassium iodide solution: Dissolve 20 g KI in 100 ml deionized distilled water.
2. Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 ml conc HCl.
3. Zinc slurry: Add 50 g zinc metal dust (200 mesh) to 100 ml deionized distilled water.
4. Diluent: Add 100 ml 18N H_2SO_4 and 400 ml concentrated HCl to 400 ml deionized distilled water in a 1-liter volumetric flask and bring to volume with deionized distilled water.

5. Arsenic Solutions:

   a. Stock arsenic solution, (1000 mg/liter): Dissolve 1.3203 g arsenic trioxide, As_2O_3, in 100 ml distilled water containing 4 g NaOH. Acidify with 20 ml concentrated HNO_3 and dilute to 1000 ml with deionized distilled water (1 ml = 1 mg As).

   b. 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/l (1 ml = 10 ug As).

   c. 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/l (1 ml = 1 ug (As).

6. Concentrated nitric acid, J.T. Baker Chemical Co. Ultrex grade or equivalent.

7. Concentrated sulfuric acid, J.T. Baker Chemical Co. Ultrex grade or equivalent.

Apparatus

1. Atomic Absorption Spectrophotometer with Boling burner.

2. Flow meter, capable of measuring 1 liter/minute, such as that used for auxiliary argon.[1]

3. Medicine dropper, capable of delivering 1.5 ml, fitted into a size "0" rubber stopper.

4. Reaction flask, a pear-shaped vessel with side arm and 50 ml capacity, both arms having 14/20 joint.[1]

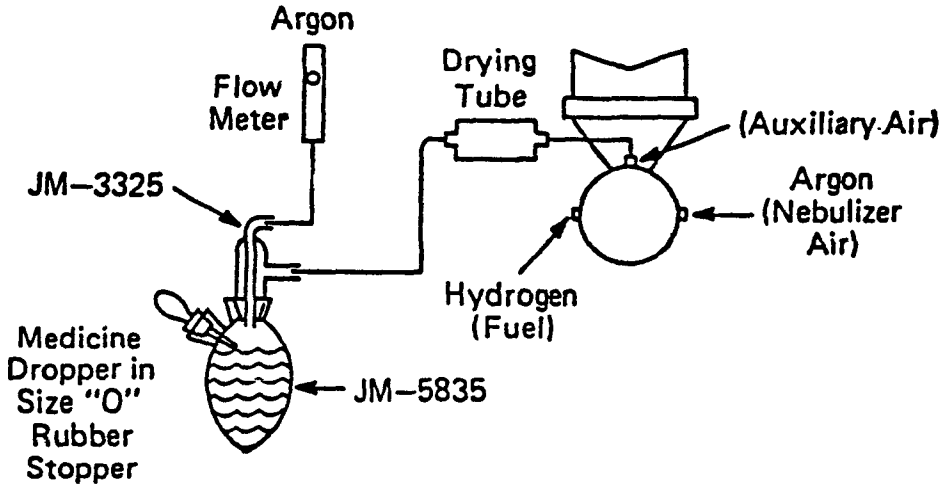
5. Special gas inlet-outlet tube, constructed from a micro

[1]Gilmont No. 12 or equivalent.

cold finger condenser[2] by cutting off the portion below the 14/20 ground glass joint.

6. Magnetic stirrer, strong enough to homogenize the zinc slurry.
7. Drying tube, 10 cm polyethylene tube filled with glass wool to keep particulate matter out of the burner.

Apparatus Set-Up



1. Assemble the apparatus as shown above.
2. Connect the outlet of the reaction vessel to the auxiliary oxidant input of the burner with tygon tubing.
3. Connect the inlet of the reaction vessel to the outlet side of the auxiliary oxidant (Argon supply) control valve of the instrument.

Procedure

1. To a 50 gm 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 concentrated HNO_3 and 12 ml 18 N H_2SO_4. Evaporate the sample in the hood on an electric hot

[1]Scientific Glass JM-5835 or equivalent.

2Scientific Glass JM-3325 or equivalent.

plate until white 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 HNO_3. Continue to add additional 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 SO_3 fumes the digestion is complete. Cool the sample, add about 25 ml distilled deionized water and again evaporate until 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 a volume with distilled deionized water.

2. Prepare working standards from the standard Arsenic solution under Reagents (5c). Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 ml standard to 100 ml volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20 and 25 ug As/liter.
3. Take the 15, 20, and 25 mg/liter standards and transfer quantitatively 25 ml from each into separate 50 ml volumetric flasks. Add to each 10 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.
4. Add 10 ml of prepared sample to a 50 ml volumetric flask. Bring to volume with distilled deionized water

containing 1.5 ml HNO_3 per liter. This is the blank.

Note: The absorbance from the blank, will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

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 $SnCl_2$ 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. Caution must be taken to avoid inhaling arsine gas.

Instrument Operation

Fuel: Argon-hydrogen flame

Wavelength: 193.7 nanometer

Optimium Concentration Range: 2-20 ug As/liter

Lower Detection Limit: 2 ug/liter

1. Turn on the Argon and adjust the flow rate to about 8 liters/minute, with an auxiliary Argon flow of 1 liter/minute.

2. Turn on the hydrogen, adjust flow rate to about 7 liters/minute and ignite. The flame is colorless. The hand may be passed 1 ft above the burner to detect heat, in order to insure ignition.

Follow the instructions given with the Atomic Absorption Spectrophotometer.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as described in Section 8.49. The extrapolated value will be 1/10 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.52

BARIUM

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of Barium in a waste or an Extraction Procedure Extract.

Summary of Method

The sample is digested using nitric and/or hydrochloric acids and the concentration of Barium measured using either a flame or graphite furnace equipped atomic absorption spectrophotometer. The flame method is most accurate when employed with solutions containing 1-20 mg Ba/liter while the graphite furnace procedure is best suited for solutions containing 10-200 ug Ba/liter.

Precaution

Barium affects the heart muscle. A dose of 550 to 600 mg is considered fatal to man. Afflictions resulting from ingestion, inhalation or absorption involve the heart, blood vessels and nerves.

Interferences

If a nitrous oxide-acetylene flame is used with Direct Aspiration chemical interferences are virtually eliminated. In this method Potassium (1000 mg/l) is added to prevent ionization of barium in this flame. If the air-acetylene flame must be used then the presence of phosphate, silicon and aluminum will lower the barium absorbance. This may be overcome by addition of lanthanum.

The graphite furnace method is sensitive to the presence of chlorides and dissolved solids.

Direct Aspiration Method

Reagents

1. 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.
2. Acetylene, should be of high purity. Acetone, which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing the cylinder when its pressure has fallen to 100 psig.
3. Deionized distilled water: Use deionized distilled water for the preparation of all reagents and calibration standards, and as dilution water.
4. Hydrochloric acid, HCl, concentrated, Ultrex grade.
5. Nitric acid, HNO_3, concentrated, Ultrex grade.
6. Nitrous oxide, commercially available cylinders.
7. Potassium Chloride solution: Dissolve 95 g KCl in distilled deionized water and bring to volume in a 1 liter volumetric flask.
8. Lanthanum Chloride solution if needed. Dissolve 25 g, reagent grade, La_2O_3 slowly in 250 ml concentrated. HCl. (Reaction is violent.) Dilute to 500 ml with distilled deionized water.
9. Barium Standard Stock Solution

1000 mg/liter solution may be purchased or prepared as follows: Dissolve 1.7787 g barium chloride dihydrate, ($BaCl_2 \cdot 2H_2O$), analytical, reagent grade, in about 200 ml distilled deionized water. Add 1.5 ml conc. HNO_3. Add to 1 liter volumetric flask and bring to volume. 1 ml = 1 mg Ba.

Apparatus

1. Atomic Absorption Spectrophotometer with nitrous oxide burner head with 2" slot. Note: A razor blade is required to dislodge, about every 20 minutes, the carbon crust that forms along the slot surface.
2. T-junction valve for rapidly changing from nitrous oxide to air, so the flame can be turned on or off with air as oxidant to prevent flashbacks.

Procedure

1. Sample preparation
   a. Transfer 100 ml of sample to a 250 ml beaker and add 3 ml concentrated HNO_3. Place it on a hot plate and evaporate to near dryness, slowly, so that the sample does not boil. Cool the beaker and add another 3 ml HNO_3. Cover with a watch glass and return to the hot plate. Continue heating gently, and add acid as necessary until the material is light in color. Evaporate to near dryness and cool. Add 2 ml of 1:1 HCl and warm the beaker to dissolve any precipitate. Wash down the beaker and watch glass with distilled

deionized water and transfer quantitatively to a 100 ml volumetric flask, add 2 ml Potassium Chloride solution and bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

Note: If air-acetylene is being used add 4.7 ml lanthamum chloride solution before bringing to volume.

b. If insoluble silicates or other material is present the sample must be filtered or centrifuged and the supernatant sampled.

2. Prepare working standards from the Standard Stock Solution. If it is desired to bracket the optimum concentration range the following is suggested:

a. Transfer 0, 0.1, 0.5, 1.0, 1.5, and 2 ml of Standard Stock Solution to 100 ml volumetric flasks. Add 2 ml potassium chloride solution. If lanthanum chloride was added to the sample, 4.7 ml must be added to the standards. Bring to volume with distilled deionized water containing 1.5 ml concentrated HNO_3/liter. The concentrations of these standards will be 0, 1, 5, 10, 15 and 20 mg Ba/liter.

Standard Addition

1. a. Take the 5, 10, and 15 mg standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample and 0.06 ml KCl solution. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Add 0.16 ml KCl solution and bring to volume with distilled deionized water containing 1.5 ml HNO_3 per liter. This is the blank.

Note: The graph peak from the blank will be 1/5 that produced by the prepared sample. The peaks from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 553.6 nanometers

Fuel: acetylene

Oxidant: Nitrous Oxide

Type of flame: Fuel rich

Optimum Concentration Range: 1-20 mg/liter Lower Detection Limit: 0.1 mg/liter

Follow the instructions given with the Atomic Absorption Spectrophotometer. The following is included as a guide:

a. Install a nitrous oxide burner head.

b. Turn on the acetylene (without igniting the flame), and adjust the flow rate to the value specified by the manufacturer for a nitrous oxide-acetylene flame.

c. Turn off the acetylene.

d. With both air and nitrous oxide supplies turned on, set the T junction valve to nitrous oxide and adjust

the flow rate according to the specifications of the manufacturer.

e. Turn the switching valve to the air position and verify that the flow rate is the same.

f. Turn the acetylene on and ignite to a bright yellow flame.

g. With a rapid motion, turn the switching valve to nitrous oxide. The flame should become rose-red; if it does not, adjust fuel flow to obtain a red cone in flame.

h. Atomize deionized distilled water containing 1.5 ml conc. HNO_3/l and check the aspiration rate. Adjust if necessary to a rate between 3 and 5 ml/min.

i. Atomize a 1-mg/l standard of the metal and adjust the burner (both sideways and vertically) in the light path until maximum response is obtained.

j. The instrument is now ready to run standards and samples.

k. To extinguish the flame, turn the switching valve from nitrous oxide to air, and turn off the acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene.

Quantification

The absorbance of spiked samples and blank vs. concentrations are plotted according to the Method of Standard Additions defined in Section 8.49. The extrapolated value will be 1/5

the concentration of the original sample. If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Graphite Furnace

Reagents

1. Barium Standard Stock Solution 1000 mg/liter solution may be purchased or prepared as follows: Dissolve 1.7787 g barium chloride dihydrate, $BaCl_2 \cdot 2H_2O$ analytical reagent grade, in about 200 ml distilled deionized water. Add 1.5 ml concentrated HNO_3 and bring to volume in a 1 liter volumetric flask. 1 ml = 1 mg Ba.
2. Concentrated Nitric Acid

Procedure

Sample Preparation

(Note: All chloride and hydrochloric acid is avoided.)

1. a. Transfer 100 ml of sample to a 250 ml beaker and add 3 ml concentrated HNO_3. Place it on a hot plate and evaporate to near dryness, slowly, so that the sample does not boil. Cool the beaker and add another 3 ml HNO_3. Cover with a watch glass and return to the hot plate. Continue heating gently, and add acid as necessary until the material is light in color. Evaporate to near dryness and cool. Add a small quantity of 1:1 HNO_3 and warm the beaker to dissolve any precipitate.

Wash down the beaker and watch glass with distilled deionized water and transfer quantitatively to a 100 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

b. If insoluble silicates or other material is present the sample must be filtered or centrifuged and the supernatant sampled.

2. a. Prepare working standards from the Standard Stock Solution. If it is desired to bracket the optimum concentration range the following is suggested:

b. Transfer 1 ml stock solution to a 1 liter volumetric flask. Bring to volume with distilled deionized water acidified with 1.5 ml conc. HNO_3/liter. Concentration: 1000 ug Ba/liter.

c. Transfer 0, 5, 10, 15, and 20 ml from a) to separate 100 ml volumetric flasks and bring to volume with distilled deionized water acidified with 1.5 ml concentrated HNO_3/liter. The concentrations of these working standards will be 0, 50, 100, 150, and 200 ug Ba/liter.

Standard Addition

1. a. Take the 100, 150, and 200 ug standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

b. Add 2 ml of prepared sample to a 10 ml volumetric

flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3 per liter. This is the blank.

Note: The absorbance of the blank will be 1/5 that produced by the prepared sample. The absorbance of the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 553.6 nanometers

Optimum Concentration range: 10 - 200 ug/liter Lower Detection limit: 2 ug/liter

Drying time and temperature: 30 seconds at 125°C

Ashing time and temperature: 30 seconds at 1200°C

Atomizing time and temperature: 10 seconds at 2800°C

Purge gas: Argon. Do not use nitrogen.

These conditions are based on a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Quantification

The absorbance of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in Section 8.49. The extrapolated value will be the concentration of the original sample.

If the plot does not result in a straight line a non-

linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.53

CADMIUM

Scope and Application

The following procedures are approved methods for determining the concentration of Cadmium in a waste or Extraction Procedure Extract.

Precaution

Cadmium is highly toxic. Minute quantities are suspected of causing adverse changes in human kidneys.

Cadmium is particularly susceptible to contamination of the work area. Special care should be taken in the handling of the material.

Comments

Two Atomic Absorption methods are described.

1. Direct Aspiration

   This method is suitable for higher concentrations (0.05-2 ug/liter optimum).

2. Graphite Furnace

   This method is suitable for lower levels (0.5-10 ug/liter optimum).

Direct Aspiration

Reagents

1. Air free of oil, water, and other foreign substances. The source may be purified air from a compressor or a cylinder of industrial grade compressed air.

2. Acetylene, standard commercial grade. Acetone, which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 7 kg/cm^2 (100 psig) acetylene.
3. Nitric Acid, concentrated, ACS.
4. Cadmium Standard Stock Solution (1000 mg/liter): Carefully weigh 3.1368 g Cadmium Sulfate Octahydrate ($Cd\ SO_4.8\ H_2O$), analytical reagent grade, and dissolve in distilled deionized water containing 1.5 ml HNO_3/liter. Transfer quantitatively to a 1 liter volumetric flask and bring to volume with the same water. 1 ml = 1 mg Cd.
5. Hydrochloric acid solution: Dilute concentrated HCl (ACS) 1:1 with distilled deionized water.

Procedure

Sample Preparation

1. Transfer 100 gm of well-mixed sample (use 100 ml when analyzing an EP extract) to a 250 ml beaker. Add 3 ml concentrated HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, so that the sample does not boil. Cool, and add another 3 ml concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 5 ml of 1:1 HCl and warm the beaker just to dissolve any precipitates.

b. Cool and bring to 100 ml with distilled deionized water.

2. If particulates such as silicates remain in the sample it must be centrifuged and the supernatant aspirated.

3. Prepare working standards from stock solution. If it is desired to work in the optimum concentration range the following is suggested:

   a. Transfer 10 ml stock solution to a 100 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml concentrated HNO_3/ liter. Concentration: 100 mg/liter.

   b. Transfer 0, 0.1, 0.5, 1.0, 1.5, and 2.0 ml solution from a) to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter. The concentrations of these standards will be 0, 0.1, 0.5, 1.0, 1.5, and 2.0 mg Cd/liter.

Standard Addition

   a. Take the 1.0, 1.5, and 2.0 mg/liter standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

   b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water containg 1.5 ml HNO_3 per liter. This is the blank.

Note: The absorbance from the blank will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 228.8 nanometers

Optimum Concentration Range: 0.05 - 2 mg/liter

Lower Detection Limit: 0.005 mg/liter

Fuel: Acetylene

Oxidant: air

Type of flame: oxidizing.

A general outline for instrument operation is given in Section 8.49. Follow the manufacturer's instructions for the Spectrophotometer being used.

Quantification

The absorbance of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in Section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Graphite Furnace

Reagents

1. Cadmium Standard Stock Solution (1000 mg/liter). Carefully weigh 3.1368 g Cadmium Sulfate Octahydrate ($CdSO_4.8H_2O$), analytical reagent grade, and dissolve in distilled deionized water containing 5 ml concentrated HNO_3/liter. Transfer quantitatively to a 1 liter volumetric flask and bring to volume with the same water. 1 ml = 1 mg Cd.
2. Concentrated HNO_3 (ACS)
3. Concentrated HNO_3 diluted 1:1 with distilled deionized water.
4. Ammonium phosphate solution (40%) Dissolve 40 grams Ammonium mono hydrogen phosphate, $(NH_4)_2HPO_4$, analytical reagent grade, in distilled deionized water and bring to 100 ml.

Procedure

1. Sample Preparation
   a. Transfer 100 gm of well-mixed sample (or when analyzing an EP extract 100 ml) to a 250 ml beaker. Add 3 ml concentrated HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, so that the sample does not boil. Cool, and add another 3 ml concentrated HNO_3. Cover the beaker with a watch glass, and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of concentrated HNO_3 until the

sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 1 ml of 1:1 HNO_3 and warm the beaker just to dissolve any precipitates. Cool the beaker.

b. Add 2 ml Ammonium phosphate solution and bring to 100 ml with distilled deionized water.

2. If particulates such as silicates remain in the sample it must be centrifuged and the supernatant sampled.

3. Prepare working standards from the stock solution. If it is desired to work in the optimum concentration range the following is suggested:

a. Transfer 1 ml stock solution to a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 5 ml concentrated HNO_3/liter. Concentration: 1000 ug/liter.

b. Transfer 10 ml from a) to a 100 ml volumetric flask and bring to volume with distilled deionized water containing 5 ml HNO_3/liter. Concentration: 100 ug/liter.

c. Transfer 0, 0.5, 1.0, 2.5, 5.0, and 10 ml from b) to 100 ml volumetric flasks. Add 2 ml Ammonium phosphate solution. Bring to volume with distilled deionized water containing 5 ml HNO_3/liter. The concentrations of these working standards will be 0, 0.5, 1.0, 2.5, 5.0, and 10 ug Cd/liter.

Standard Addition

1. a. Take the 2.5, 5.0 and 10 ug/liter standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample and 0.06 ml ammonium phosphate solution. Bring to volume with distilled deionized water.

   b. Add 2 ml of prepared sample to a 10 ml volumetric flask and add 0.16 ml ammonium phosphate solution. Bring to volume with distilled deionized water. This is the blank.

Note: The absorbance from the blank will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimium absorbance can be judged.

Instrument Operation

Wavelength: 228.8 nanometers

Optimum Concentration Range: 0.5 - 10 ug/liter

Lower Detection Limit: 0.1 ug/liter

Purge Gas: Argon

Drying time and temperature: 30 sec at 125°C

Ashingtime and temperature: 30 sec at 500°C

Atomizing time and temperature: 10 sec at 1900°C

These conditions are based on a 20 ul injection continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer

model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Quantification

The absorbance of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in Section 4.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.54

CHROMIUM

Scope and Application

The following procedures are approved methods for determining the concentration of chromium in an Extraction Procedure Extract, an industrial liquid waste, or landfill liquid component or leachate.

Precaution

Hexavalent chromium is both acutely toxic and carcinogenic to man. While the trivalent form is less toxic to humans, care should be exercised in its handling.

Summary of Method

The sample is digested using nitric and/or hydrochloric acids and the concentration of chromium measured using either a flame or graphite furnace equipped atomic absorption spectrophotometer. The flame method is most acurate when employed with solutions containing 0.5-10 mg Cr/liter while the graphite furnace procedure is best suited for solutions containing 5-100 ug Cr/liter.

Comments

1. The direct aspiration method is suitable for a concentration range of 0.5-10 mg/l. The nitrous oxide-acetylene flame is recommended bacause, while less sensitive, it eliminates interferences from other common metals such as iron and nickel. If the air-acetylene flame must be used it should be lean. Interference from other ions has reportedly been overcome by addition of ammonium biflouride.

2. In the furnace method the presence of calcium interferes. However, since at concentrations above 200 mg/l its effect becomes constant, it is added to insure this minimum level. Hydrogen peroxide is used to bring all chromium present in the sample to the +6 state.

Direct Aspiration

Reagents

1. Nitrous oxide, commercially available cylinders
2. Acetylene should be of high purity standard commercial grade.
3. Concentrated Nitric Acid (HNO_3)
4. Chromium Stock Solution (1000 mg/liter):
   Dissolve 1.9231 grams chromium trioxide (CrO_3) analytical reagent grade, in deionized distilled water. Add 1.5 ml HNO_3 and bring to volume in a 1 liter volumetric flask with this same water (1 ml = 1 mg Cr).
5. 1% ammonium biflouride solution if needed for air-acetylene flame:
   Dissolve 0.2 grams sodium sulfate in distilled deionized water. Add 1 gram ammonium biflouride (NH_4HF_2). Bring to volume in a 100 ml volumetric flask with distilled deionized water.

Apparatus

1. Atomic Absorption Spectrophotometer with nitrous oxide burner head with 2" slot.
2. T-junction valve for rapidly changing from nitrous oxide to air, so the flame can be turned on or off with air as oxidant to prevent flashbacks.

Procedure

Sample preparation

1. a. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, taking care not to let the sample boil. Cool, and add another 3 ml conc HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 1 ml HNO_3 and warm the beaker until any precipitates present dissolve.

   b. Cool and bring to 100 ml with distilled deionized water.

   Note: If the air-acetylene flame is used add 1 ml ammonium biflouride solution just before making up to 100 ml volume.

2. If particulates, such as silicates, remain in the digested sample, then centrifuge the digestate and only aspirate the supernatant.

3. Prepare working standards from stock solution. To bracket the optimum concentration range the following is suggested:

   a. Transfer 0, 0.1, 0.2, 0.5, 0.8, and 1.0 ml stock solution to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter. These working standards will contain 0, 1, 2, 5, 8 and 10 mg Cr/liter.

Note: If the air-Acetylene flame must be used add 1 ml ammonium biflouride solution just before making up to 100 ml volume.

4. Standard Addition

a. Take the 5, 8, and 10 mg standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3 per liter. This is the blank.

Note: The absorbance from the blank (b), will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 357.9 nanometers

Optimum concentration range: 0.5-10 mg/liter

Lower detection limit: 0.05 mg/liter

Fuel: Acetylene

Oxident: Nitrous Oxide

Type of Flame: Fuel rich

Follow the instructions given with the Atomic Absorption Spectrophotometer. The following is included as a guide:

a. Install a nitrous oxide burner head.

b. Turn on the acetylene (without igniting the flame), and adjust the flow rate to the value specified by the manufacturer for a nitrous oxide-acetylene flame.

c. Turn off the acetylene.

d. With both air and nitrous oxide supplies turned on, set the T-junction valve to nitrous oxide and adjust the flow rate according to the specifications of the manufacturer.

e. Turn the switching valve to the air position and verify that the flow rate is the same.

f. Turn the acetylene on and ignite to a bright yellow flame.

g. With a rapid motion, turn the switching valve to nitrous oxide. The flame should become rose-red; if it does not, adjust fuel flow to obtain a red cone in flame.

h. Atomize deionized distilled water containing 1.5 ml conc. HNO_3/l and check the aspiration rate. Adjust if necessary to a rate between 3 and 5 ml/min. Atomize a 1 mg/l standard of the metal and adjust the burner (both sideways and vertically) in the light path until maximum response is obtained. The instrument is now ready to run standards and samples.

i. To extinguish the flame, turn the switching valve from nitrous oxide to air, and turn off the acetylene. This procedure eliminates the danger of flashback that may occur on direct ignition or shutdown of nitrous oxide and acetylene.

Quantification

The absorbance of spiked samples and blank vs the concentration are plotted according to the Method of Standard Additions as defined in General Requirements #11. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Graphite Furnace

Reagents

1. Chromium Standard Stock Solution (1000 mg/liter):
   a. Dissolve 1.9231 grams Chromium trioxide (CrO_3) analytical reagent grade, in deionized distilled water. Add 5 ml HNO_3 and bring to volume in a 1 liter volumetric flask with this same water (1 ml = 1 mg Cr).
2. Concentrated HNO_3
3. Calcium nitrate solution:
   Dissolve 11.8 grams Calcium nitrate tetrahydrate ($Ca(NO_3)_2.4H_2O$), analytical reagent grade in deionized distilled water and dilute to 100 ml (1ml = 20mg Ca).
4. 30% hydrogen peroxide

Procedure

Sample Preparation

1. a. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc HNO_3. Place the beaker on a hot plate and evaporate to near dryness, taking care not to let the sample boil. Cool, and add another 3 ml conc HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 1 ml of 1:1 HNO_3 and warm the beaker until any precipitate present dissolves. Cool the beaker.

b. Add 1 ml of 30% hydrogen peroxide and 1 ml Calcium nitrate solution. Transfer to a 100 ml flask and bring to volume with distilled deionized water.

2. If any particulates such as silcates remain in the digested sample, then centrifuge the digestate and only aspirate the supernatant.

3. Prepare working standards from stock solution: To bracket the optimum working range the following is suggested:

   a. Transfer 1 ml stock solution to a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 5 ml HNO_3/liter. Concentration 1000ug/liter.

   b. Transfer 0, 1, 2.5, 5, 7.5 and 10 ml from a) to separate 100 ml volumetric flasks. Add 1 ml 30% hydrogen peroxide and 1 ml calcium nitrate solution. Bring to volume with distilled deionized water containing 5 ml HNO_3/liter. The concentrations of these working standards are 0, 10, 25, 50, 75, and 100 ug Cr/liter.

Standard Addition

1. a. Take the 50, 75, and 100 ug standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Add 0.03 ml $CaNO_3$ solution and 0.03 ml H_2O_2 solution. Bring to volume with distilled deionized water.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Add 0.08 ml $CaNO_3$ solution and 0.08 ml H_2O_2 solution. Bring to volume with distilled deionized water. This is the blank.

Note: The absorbance from the blank (b), will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 357.9 nanometers

Optimum Concentration Range: 5-100 ug/liter

Lower detection limit: 1 ug/liter

Purge gas: Argon

Drying time and temp.: 30 secs-125°C

Ashing time and temp.: 30 secs-1000°C

Atomizing time and temp.: 10 secs-2700°C

The conditions listed above are based on a 20 ul injection; continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Quantification

The absorbances of spiked samples and blank vs concentrations are plotted according to the Method of Standard Additions as defined in General Requirements #11. The extrapolated

value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8:56

LEAD

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of Lead in a waste or an Extraction Procedure Extract.

Precaution

Lead is poisonous and accumulates in the body. Drinking water does not usually contain more than 20 ug/liter. It can be leached from old lead plumbing by acid water.

Summary of Method

The sample is digested using nitric and/or hydrochloric acids and the concentration of lead measured using either a flame or graphite furnace equipped atomic absorption spectrophotometer. The flame method is most accurate when employed with solutions containing 1-20 mg Pb/liter while the graphite furnace procedure is best suited for solutions containing 5-100 ug Pb/liter.

Comments

1. Two wavelengths are suitable and may be tested for best operating conditions. The 217.0 nm wavelength is more sensitive but may produce more background noise.
2. The Graphite Furnace method is susceptible to sulfate interference. Up to 1500 ppm sulfate can be suppressed by addition of Lanthanum.

3. Contamination of the working environment is a special problem. All glassware should be cleaned immediately prior to use and then covered.

Direct Aspiration

Reagents

1. 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. Breathing quality air can cause flashback.
2. Acetylene should be of high quality grade. Avoid "purified grade" acetylene. Acetone, which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 7 kg/cm^2 (100 psig) acetylene.
3. Nitric Acid conc.
4. Lead Standard Stock Solution 1000 mg/liter stock solution may be purchased or prepared as follows: Dissolve 1.5985 g lead nitrate ($Pb(NO_3)_2$) analytical reagent grade, in about 200 ml distilled deionized water. Acidify with 10 m l conc. HNO_3 and bring to volume in a 1 liter volumetric flask. (1 ml = 1 mg Pb.)
5. Hydrochloric acid solution: Dilute conc. HCl 1:1 with distilled deionized water.

Procedure

Sample Preparation

1. a. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, in order to keep the sample from boiling. Cool, and add another 3 ml conc. HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 5 ml of 1:1 HCl and warm the beaker just to dissolve any precipitates.

   b. Cool and bring to 100 ml with distilled deionized water.

2. If particulates such as silicates remain in the sample it must be centrifuged and the supernatant aspirated.

3. Prepare working standards from stock solution. If it is desired to work in the optimum concentration range the following is suggested:

   a. Transfer 0, 0.1, 0.5, 1.0, 1.5, and 2.0 ml of stock solution to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter. The concentrations of these working standards are 0, 1, 5, 10, 15, and 20 mg Pb/liter.

Standard Addition

1. a. Take the 10, 15, and 20 mg standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

   b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3 per liter. This is the blank.

   Note: The absorbance from the blank (b), will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 283.3 nanometers
217.0 nanometers (more sensitive)

Optimum Concentration Range: 1-20 mg/liter

Lower Detectable limit: 0.1 mg/liter Fuel: Acetylene

Oxidant: Air

Type of flame: Oxidizing

This method is especially sensitive to turbulance in the flame. Special care should be taken to position the burner so that the light beam passes through the most

stable center portion of the flame. The absorbance should be maximized with a lead standard.

A general outline for instrument operation is given in Section 8.49. Follow the manufacturer's instructions for the Spectrophotometer being used.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in Section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a nonlinear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Graphite Furnace

Reagents

1. Lead Standard Stock Solution 1000 mg/liter stock solution may be purchased or prepared as follows: Dissolve 1.5985 g lead nitrate ($Pb(NO_3)_2$) analytical reagent grade, in about 200 ml distilled deionized water. Acidify with 10 ml conc HNO_3 and bring to volume in a 1 liter volumetric flask. 1 ml = 1 mg Pb.
2. Concentrated HNO_3
3. Lanthanum Nitrate Solution: Dissolve 58.64 g analytical reagent grade Lanthanum oxide ($La_2 O_3$) in 100 ml conc. HNO_3 and dilute to 1000 ml with distilled deionized water. 1 ml = 50 mg La.

Procedure

Sample Preparation

1. a. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc. HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, so that the sample does not boil. Cool, and add another 3 ml conc. HNO_3. Cover the beaker with a watch glass, and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 1 ml of 1:1 HNO_3 and warm the beaker just to dissolve any precipitates. Cool the beaker. Add 10 ml of Lanthanum nitrate

solution and bring to volume in a 100 ml volumetric flask using distilled deionized water.

2. If particulates such as silicates remain in the sample it must be centrifuged and the supernatant sampled.
3. Prepare working standards from the Stock solution. If it is desired to work in the optimum concentration range the following is suggested:
   a. Transfer 1 ml stock solution to a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 5 ml conc. HNO_3/liter. Concentration: 1000 ug/liter.
   b. Transfer 0, 0.5, 2.5, 5.0, 7.5, and 10 ml from (a) to separate 100 ml volumetric flasks. Add 10 ml Lanthanum Nitrate solution and bring to volume using distilled deionized water. The concentrations will be 0, 5, 25, 50, 75, and 100 ug/liter.

Standard Addition

1. a. Take the 50, 75, and 100 ug standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Add 0.8 ml lanthanum nitrate solution and bring to volume with distilled deionized water.
   b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Add 0.8 ml lanthanum nitrate solution and bring to volume with distilled deionized water. This is the blank.

Note: The absorbance from the blank (b), will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimium absorbance can be judged.

Instrument Operation

Wavelength: 283.3 nanometers
217.0 nanometers

Optimum concentration range: 5-100 ug/liter

Lower detection limit: 1 ug/liter.

Purge gas: Argon

Drying time and temp: 30 sec - 125°C

Ashing time and temp: 30 sec - 500°C

Atomizing time and temp: 10 sec - 2700°C

The 217.0 nanometer wavelength is more sensitive. The electrodeless discharge lamp has been reported helpful at this wavelength. The sample may also be successfully atomized at a lower temperature. (2400°C)

The conditions listed above are based on a 20 ul injection; continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard

Additions as defined in Section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a nonlinear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.57

MERCURY

Scope and Application

The flameless, cold vapor, atomic absorption procedure is approved for use in determining the concentration of mercury in an Extraction Procedure Extract, a RCRA waste, or landfill leachate.

Precaution

The extreme toxicity of mercury is well known. Care should be taken in the handling of materials and to avoid breathing any vapors. A trap should be constructed to receive the exhaust gas.

Summary of Method

The sample is pretreated to break down organic mercury compounds, and the mercury is then reduced to the zero oxidation state. In this form it is swept from the solution by a purge gas and enters a glass or plastic absorption cell. This cell has been aligned with the light beam from the mercury hollow cathode lamp in the atomic absorption spectrophotometer, and the mercury absorption is proportional to the concentration.

Comments

1. The method is subject to interference from sulfide above 20 mg/l. Oxidation with potassium permanganate can be used to remove this interference.

2. Chloride containing wastes require excess permanganate for removal. Chlorine gas is generated and must be purged from the sample before analysis.
3. Copper may also interfere. It is expected that the Method of Standard Addition will compensate for this.
4. In this method it is possible that some organic substance will not be oxidized and will absorb at the given wavelength. In this case, a second sample can be prepared and analyzed without adding any stannous sulfate to reduce the mercury. The true mercury value can then be found from the difference.
5. Disposal of residues:
   The wastes from mercury analyses can be saved and treated to recover the mercury. (See "Disposal".) The contaminated mercury may be returned to the manufacturer for recycling.

Apparatus

1. An atomic absorption spectrophotometer with an open presentation area so that the cold vapor cell may be attached to it.
2. Absorption cell 10 cm. long and about 1" diameter; composed of glass or plexiglass and having quartz end windows.
3. Air pump capable of delivering 2 liters of air/minute with rotameter for monitoring air flow.
4. Tygon aeration tubing and glass tube with fritted end (coarse porosity glass).
5. Drying tube 6" x 3/4" dia. containing 20 grams magnesium perchlorate.

6. 60 W light bulb positioned to shine on the absorption cell so that the temperature is maintained 10°C above ambient. This prevents condensation by moisture. If the drying tube is used this may not be necessary.
7. Scrubber bottle containing a glass frit immersed in absorbing solution:
   a. 1 part 0.1 molar potassium permanganate to 1 part 10% sulfuric acid. or
   b. 3% potassium iodide solution containing 0.25% iodine.

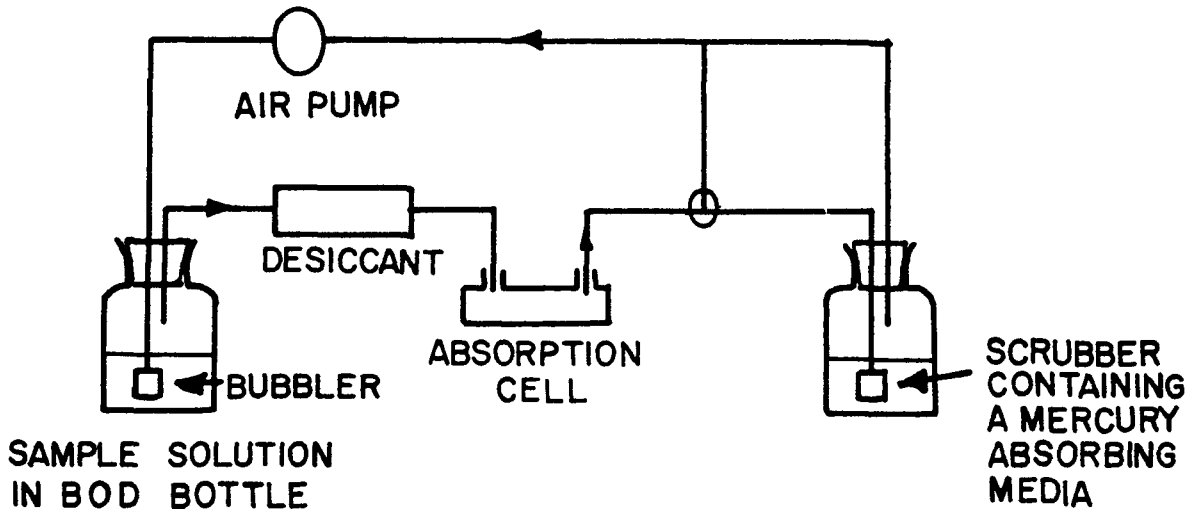


Figure 8.57-1
FLAMELESS MERCURY A.A. SET-UP

Procedure

1. Assemble equipment as in the diagram.
2. Set the wavelength at 253.7 nanometer.
3. Install the absorption cell and align it in the light beam using 2 cards, each having a 1" diameter hole. These are placed over the ends of the cell for ease in centering the beam.
4. Turn on the air and adjust flow rate to 1 liter/minute. and allow the air to flow continuously.
5. Follow manufacturer's instructions for instrument warm up and operation.
6. Prepare working standards from stock solution:
   To bracket the optimum concentration range (0.2-10 ug/liter) the following is suggested:
   a. Transfer 1 ml of stock solution to a 1 liter volumetric flask and bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter. Concentration: 1000 ug/liter. (1 ml = 1 ug Hg)
   b. Transfer 0, 1, 2, 5, 8, and 10 ml from a. to separate 100 ml volumetric flasks and bring to volume with distilled deionized water containing 1.5 ml HNO_3/ liter. The concentrations of these working standards will be 0, 10, 20, 50, 80 and 100 ug Hg/liter. (10 ml aliquots transferred for analysis will contain 0, 0.1, 0.2, 0.5, 0.8, and 1.0 ug Hg.)

Reagents

1. Sulfuric acid solution (0.5N):

   Dilute 14 ml concentrated H_2SO_4 to 1 liter with distilled deionized water.

2. Nitric Acid, concentrated

3. Stannous Sulfate solution:

   Add 25 grams $SnSO_4$ to 250 ml sulfuric acid solution (0.5N). This mixture should be stirred continuously during analysis.

4. Sodium chloride - Hydroxylamine sulfate solution:

   Dissolve 12 grams NaCl and 12 grams hydroxylamine sulfate in distilled deionized water and dilute to 100 ml.

5. Potassium Permanganate solution: (5% w/v)

   Dissolve 5g $KMnO_4$ in 100 ml distilled deionized water.

6. Potassium Persulfate solution: (5% w/v) Dissolve 5g $K_2S_2O_8$ in 100 ml distilled deionized water.

7. Mercury stock solution (1000 mg/liter):

   Dissolve 0.1354 grams mercuric chloride ($HgCl_2$) in distilled deionized water containing 1.5 ml concentrated HNO_3/liter. Bring to volume in a 100 ml volumetric flask. (1 ml = 1 mg Hg.)

7. Standard Addition

   a. Take the 50, 80 and 100 ug standards and transfer quantitatively 25 ml from each into separate 50 ml volumetric flasks. Add to each 10 ml of the sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

   b. Add 10 ml of sample to a 50 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter. This is the blank.

Note: The absorbance from the blank will be 1/5 that produced by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared sample. Keeping these in mind the correct dilutions to produce optimium absorbance can be judged.

8. Treatment of sample and standards:

   a. Transfer a 10 ml aliquot to a 300 ml BOD bottle. Add distilled deionized water to make 100 ml. Add 5 ml sulfuric acid solution and 2.5 ml concentrated HNO_3. After mixing add 15 ml potassium permanganate solution. Additional permanganate may be required for some wastes. Shake and add enough so that the purple color persists for at least 15 minutes. Then add 8 ml potassium persulfate solution and heat for 2 hours in a water bath at 95°C. Cool. The sample is now fully oxidized.

b. During oxidation chlorides, if present, are converted to free chlorine which interferes in the analysis. Additionally any excess permanganate must be destroyed. Add 25 ml hydroxylamine sulfate solution and allow to stand for at least 30 seconds.

c. Purge the dead air space in the upper portion of the BOD bottle, add 5 ml well-mixed stannous sulfate solution, and immediately attach the bottle to the bubbler apparatus as in the diagram, thus forming a closed system. The pumps must run continuously. The absorbance will increase and reach a maximum within 30 seconds.

d. After about 1 minute, when measurement is complete, open the bypass valve and allow the gas to flow through the mercury trap. When absorbance returns to baseline remove the sample bottle and replace it with a BOD bottle containing distilled deionized water. Flush the system for a few minutes. Close the valve and run the next sample or standard.

Quantification

The absorbances of spiked samples and blank vs. the number of micrograms mercury are plotted according to the Method of Standard Addition as defined in Section 8.49. If the additions were made as suggested in the method, the extrapolated value will be the number of micrograms contained

in 2 ml of the sample. From this the concentration in the original sample can be calculated.

If the plot does not result in a straight line, a non-linear interference is present. This can sometimes be overcome by dilution.

APPENDIX

DISPOSAL OF IONIC MERCURY IN SOLUTION

1. Bring the pH of the solution to neutral or basic by adding sodium carbonate. Sodium hydroxide may have to be added if neutralization cannot be achieved with sodium carbonate.
2. Add granular zinc or magnesium as follows: For every 100 grams of either mercurous or mercuric chloride present in the solution, add 110 grams zinc or 40 grams magnesium. This achieves a 4 molar excess.
3. Stir the solution for 24 hours in a hood. CAUTION: Hydrogen gas will be released during this process.
4. After 24 hours the solid material (mercury amalgam) will have separated. Decant and discard the supernatant liquid to the sewer.
5. Quantitatively transfer the solid material to a convenient container and allow to dry.

The following companies are among those that have recycled mercury in the past:

These companies may be able to supply a steel flask of 76 lbs. capacity which can be used for storage and shipment of contaminated metal.

1) Bethlehem Apparatus Co., Inc.
   Front and Depot Sts.
   Hellertown, PA 18055 Tel: (215) 838-7034

2) Goldsmith Division, National Lead Co.
111 North Wabash
Chicago, Ill. 60602 Tel: (312) 726-0232

3) Wood Ridge Chemical Corp.
Park Place East
Wood Ridge, N.J. 07075 Tel: (201) 939-4600

4) Quicksilver Products, Inc.
350 Brannon Street
San Francisco, Cal. 94107 Tel: (415) 781-1988

Method 8.58

NICKEL

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of nickel in a waste or Extraction Procedure Extract.

Summary of Methods

A sample is digested using nitric acid and the concentration of nickel is measured using either a flame or graphite furnace equipped atomic absorption spectrophotometer. The flame method is most accurate when employed with solutions containing 0.3-5 mg Ni/liter, while the graphite furnace procedure is best suited for solutions containing 5-100 mg/Ni liter.

Direct Aspiration

Reagents

1. 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.
2. Acetylene should be of high purity. Acetone, which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 7 kg/cm^2 (100 psig) acetylene.
3. Nitric acid, concentrated
4. Nickel Standard Stock solution, (1000 mg/liter): Dissolve 4.9532 g nickel nitrate hexahydrate ($Ni(NO_3) \cdot 6H_2O$), analytical reagent grade, in distilled deionized water containing 1.5 ml concentrated HN_3/liter. Bring to volume in a 1 liter volumetric flask using the same water. (1 ml = 1 mg Ni)

Procedure

Sample Preparation

1. a. Transfer 100 gms (or in the case of EP extracts and 100 ml) of well-mixed sample to a 250 ml beaker. Add 3 ml concentrated HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, so that the sample does not boil. Cool, and add another 3 ml concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as

to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 5 ml of 1:1 HNO_3 and warm the beaker in order to dissolve any precipitates.

b. Cool and bring to 100 ml with distilled deionized water.

2. If particulates such as silicates remain in the sample, it must be centrifuged and the supernatant aspirated.

3. Prepare working standards from stock solution. If it is desired to work in the optimum concentration range, the following is suggested:

a. Transfer 10 ml stock solution to a 100 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml concentrated HNO_3/liter. Concentration: 100 mg/liter.

b. Transfer 0, 0.5, 1.0, 2.0, 4.0, and 5.0 ml solution from a) to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 5 ml HNO_3/liter. The concentrations of these standards will be 0, 0.5, 1, 2, 4 and 5 mg Ni/liter.

Standard Addition

1. a. Take the 2, 4 and 5 mg/liter standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing

5 ml HNO_3 per liter.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water containing 5 ml HNO_3/liter. This is the blank.

Note: The absorbance from the blank will be 1/5 that produced by the prepared sample. The absorbance from the spiked standard will be 1/2 that produced by the standard plus the contribution from 1/5 of the prepared sample. Keeping these in mind, the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 232.0 nanometers (352.4 nm may be used. It is less susceptible to interference, but is somewhat less sensitive.)

Optimum Concentration Range: 0.3-5 mg/liter

Lower Detection Limit: 0.04 mg/liter

Fuel: Acetylene

Oxidant: Air

Type of Flame: Oxidizing

A general outline for instrument operation is given in section 8.49. Follow the manufacturer's instructions for the Spectrophotometer being used.

Quantification

The absorbance of spiked samples and blank vs. the concentrations are plotted accordng to the Method of Standard

Additions as defined in section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line, a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents, if there is some knowledge about the waste.

Graphite Furnace

Reagents

Prepare working standards and blank to bracket the range 5-100 mg Ni/liter by making appropriate dilutions of the standards described in the direct aspiration method.

Procedure

The Sample is digested, standard additions are prepared, and the analysis conducted as described under the direct aspiration method.

Instrument Operation

Wave length: 232.0 nanometers

Optimum Concentration Range: 5-100 ug/liter

Lower Detection Limit: 1.0 ug/liter

Purge Gas: Argon or nitrogen

Drying Time and Temp: 30 sec at 125° C

Ashing Time and Temp: 30 sec at 900° C

Atomizing Time and Temp: 10 sec at 2700° C

These conditions are based on a 20 ul injection, continuous flow purge gas, and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Method 8.59

SELENIUM

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of selenium in a waste or an Extraction Procedure Extract. While both methods are generally aceptable for RCRA type samples, the graphite furnace method is simpler to use than the hydride. However it is sensitive to chloride interference when the concentration is greater than 800 mg/liter. The presence of sulfate in concentrations greater than 200 mg/liter will also interfere. If it does not exceed 2000 mg/liter the sulfate can be suppressed. The hydride method requires greater preparation and is sensitive to high concentrations of chromium, copper, mercury, silver cobalt and molybdenum.

Summary of Methods

In the furnace method the sample is digested using nitric acid and hydrogen peroxide. The method is most accurate for solutions containing 5 - 100 ug Selenium/liter.

In the gaseous hydride method the sample is digested using nitric and sulfuric acids. The selenium is then reduced from the +4 to the +2 oxidation state with stannous chloride, and converted to the hydride SeH_3, using zinc metal. The hydride is swept into an argon entrained hydrogen flame for analysis.

It is most accurate when employed for solutions containing 2 - 20 ug Selenium/liter. However high concentrations of chromium, copper, mercury, silver, cobalt and molybdenum can interfere in the analysis.

Graphite Furnace Method

Reagents

1. Standard Stock Solution

   1000 ug/liter solution may be purchased, or prepared as follows:

   Dissolve 0.3453g of selenous acid (assay 94.6% H_2SeO_3) in distilled deionized water. Add to a 200 ml volumetric flask and bring to volume (1 ml = 1 mg Se).

2. Nickel Nitrate Solution, 5%

   Dissolve 24.780g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in distilled deionized water and make up to 100 ml.

3. Nickel Nitrate Solution, 1%

   Dilute 20 ml of the 5% solution to 100 ml with distilled deionized water.

4. 30% Hydrogen Peroxide

5. Sodium Hydroxide

6. Concentrated Nitric Acid

Procedure

1. Sample Preparation

   a. Transfer 100 gms(or in the case of EP extracts 100 ml) of well-mixed sample to a 250 ml beaker

and add 2 ml of 30% H_2O_2 and 1 ml of concentrated HNO_3. Heat on a hot plate for 1 hour at 95°C or until the volume is less than 50 ml.

b. If particulate material remains in the sample after oxidation, add additional HNO_3 and H_2O_2 and digest until no changes are noted in the amount of particulate matter remaining.

c. At this point cool and bring to 50 ml with distilled deionized water. The mixture should be centrifuged and only the supernatant used for the remaining steps of the analysis.

d. Transfer quantitatively 25 ml of this solution into a 50 ml volumetric flask. Add 5 ml of 1% nickel nitrate solution and bring to 50 ml with distilled deionized water.

Note: If sulfate is present at concentrations of more than 200 mg/l add 10 ml of 5% nickel nitrate solution instead of 5 ml of 1% solution.

2. Prepare standards from stock solution. The following provides standards in the optimum working range:

a. Pipet 1 ml stock solution into a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml concentrated HNO_3 per liter. The concentration of this solution is 1000 ug Se/liter (1 ml = 1 ug Se)

b. Prepare 6 working standards by transferring 0, 1.0, 2.5, 5.0, 7.5 and 10.0 ml from a. into 100 ml volumetric flasks. Add 1 ml concentrated HNO_3, 2 ml 30% H_2O_2

and 2 ml 5% nickel nitrate solution. Bring to volume with distilled deionized water. The concentrations of these working standards are 0, 10, 25, 50, 75, and 100 ug Se/liter. They are ready for injection.

Note: If sulfate is present in the sample at concentrations of more than 200 mg/l add 20 ml of 5% nickel nitrate solution instead of 2 ml before bringing to volume.

3. Standard Addition

   a. Take the 50, 75 and 100 ug/liter standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Add 0.3 ml of 1% nickel nitrate solution and 0.3 ml H_2O_2 solution. Bring to volume with distilled deionized water.

   b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Add 0.3 ml of 1% nickel nitrate solution and 0.3 ml H_2O_2 solution. Bring to volume with distilled deionized water. This is the blank.

      Note: that the absorbance from the blank will be 1/5 that producd by the prepared sample. The absorbance from the spiked standards will be 1/2 that produced by the standards alone plus the contribution from 1/5 of the prepared sample. Keeping these in mind, the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 196.0 nanometers

Optimum Concentration Range: 5 - 100 ug/liter

Lower Detection Limit: 2 ug/liter

Drying Time and Temperature: 30 seconds at 125°C

Ashing Time and Temperature: 30 seconds at 1,200°C

Atomizing Time and Temperature: 10 seconds at 2,700°C

Pure Gas: Argon

These conditions are based on a 20 ul injection, continuous flow purge gas, and non-pyrolytic graphite in a Perkin Elmer Model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

Quantification

The absorbance of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line, non-linear interference is present. This can sometimes be overcome by dilution, or additon of other reagents if there is some knowledge about the waste.

Gaseous Hydride Method

Reagents

1. Stannous Chloride Solution: Dissolve 100g $SnCl_2$ in 100 ml concentrated HCl.
2. Zinc slurry: Add 50g zinc metal dust (200 mesh) to to 100 ml deionized distilled water.
3. Diluent: Add 100 ml 18N H_2SO_4 and 400 ml concentrated HCl to 400 ml deionized distilled water in a 1-liter volumetric flask and bring to volume with deionized distilled water.
4. Standard Stock Solution: 1000 mg/liter solution may be purchased, or prepared as follows: Dissolve 0.3453g of selenious acid (assay 94.6% of H_2SeO_3) in distilled deionized water. Add to a 200 ml volumetric flask and bring to volume (1 ml = 1 mg Se).

Apparatus

1. Atomic Absorption Spectrophotometer with Boling Burner.
2. Flow Meter, capable of measuring 1 l/min, such as that used for auxiliary argon.[1]
3. Medicine Dropper, capable of delivering 1.5 ml, fitted into a size "0" rubber stopper.
4. Reaction Flask, a pear-shaped vessel with side arm and 50 ml capacity, both arms having ℨ 14/20 joint.[2]
5. Special Gas Inlet-Outlet Tube, constructed from a micro cold finger condenser[3] by cutting off the portion below the ℨ 14/20 ground glass joint.

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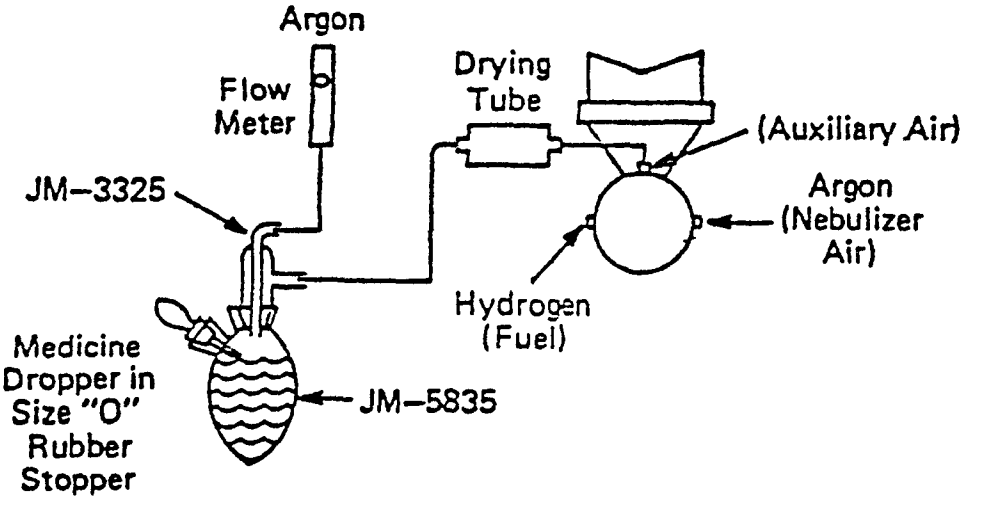
[1] Gilmont No. 12 or equivalent

[2] Scientific Glass JM-5835 or equivalent

[3] Scientific Glass JM-5325 or equivalent

6. Magnetic Stirrer, strong enough to homogenize the zinc slurry.
7. Drying Tube, 100-mm-long polyethylene tube filled with glass wool to keep particulate matter out of the burner.

Apparatus Set-Up



Connect the apparatus with the burner as shown above. Connect the outlet of the reaction vessel to the auxiliary oxidant input of the burner with tygon tubing. Connect the inlet of the reaction vessel to the outlet side of the auxiliary oxident (argon supply) control valve of the instrument.

Procedure

1. Sample Preparation

   To a 50 gm sample (or in the case of EP extracts a 50 ml sample) add 10 ml concentrated HNO_3 and 12 ml of 18 N H_2SO_4. Evaporate the sample on a hot plate until white 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 HNO_3. Maintain an excess of 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 SO_3 fumes, the digestion is complete.

   Cool the sample, add about 25 ml distilled deionized water and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 ml of concentrated HCl and bring to a volume of 100 ml with distilled deionized water.

2. Prepare working standards from the standard stock solution. The following provides standards in the optimum working range:

   a. Pipet 1 ml stock solution into a 1 liter volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/liter. (1 ml = 1 ug Se)

   b. Prepare 6 working standards by transferring 0, 0.5, 1.0, 1.5, 2.0 and 2.5 ml from a. into 100 ml volumetric

flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20 and 25 ug Se/liter.

3. Standard Additions

   a. Take the 15, 20, and 25 ug standards and transfer quantitatively 25 ml from each into separate 50 ml volumetric flasks. Add to each 10 ml of the prepared sample. Bring to volume with distilled deionized water containing 1.5 ml HNO_3/liter.

   b. Add 10 ml of prepared sample to a 50 ml volumetric flask. Bring to volume with distilled deionized water containing 1.5 ml HNO_3 per liter. This is the blank.

Instrument Operation

Fuel: Argon-hydrogen flame

Wavelength: 196.0 nanometers

Optimum Concentration Range: 2-20 ug Se/liter

Lower Detection Limit: 2 ug/liter

Turn on the argon and adjust the flow rate to about 8 liters/minute with auxiliary argon flow at 1 liter/min.

Turn on the hydrogen, adjust flow rate to about 7 liters/minute and ignite. The flame is colorless. The hand may be passed 1 ft. above the burner to detect heat, in order to insure ignition.

Follow the instructions given with the atomic absorption spectrophotometer.

Treatment of Samples and Standards

Transfer a 25-ml portion of the digested sample or standard to the reaction vessel. Add 0.5 ml $SnCl_2$ solution. Allow at least 10 minutes 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 droppper 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 part way to the base line, remove the reaction vessel.

Quantification

The spiked samples and blank vs. concentrations are plotted according to the Method of Standard Additions, as defined in section 8.49. The extrapolated value will be 1/10 the concentration of the original sample due to a dilution during preparation.

If the plot does not result in a straight line, a non-linear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Method 8.60

SILVER

Scope and Application

The following atomic absorption procedures are approved methods for determining the concentration of Silver in a waste or an Extraction Procedure Extract.

Summary of Method

The sample is digested using nitric and/or hydrochloric acids and the concentration of silver measured using either a flame or graphite furnace equipped atomic absorption spectrophotometer. The flame method is most accurate when employed with solutions containing 0.1 - 4 mg Ag/liter, while the graphite furnace procedure is best suited for solutions containing 1 - 25 ug Ag/liter.

Precaution

Silver in concentrations of 0.4 to 1 mg/liter can cause damage to liver, kidneys and spleen. Natural drinking waters do not generally contain more than 2 ug/liter.

Comments

1. Silver samples and silver nitrate standards should not be stored. Silver is light-sensitive and has a tendency to plate out on the container walls. Discard solutions after use.

2. The use of hydrochloric acid is avoided to prevent precipitation of silver chloride.

3. If plating out or AgCl formation is suspected it can be

redissolved by addition of cyanogen iodide. However, this can only be done after digestion to prevent formation of toxic hydrogen cyanide under acid conditions.

Direct Aspiration

Reagents

1. 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.
2. Acetylene should be of high purity. Acetone, which is always present in acetylene cylinders, can be prevented from entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 7 kg/cm^2 (100 psig) acetylene.
3. Concentrated Nitric Acid (HNO_3), Ultrex grade.
4. Concentrated Ammonium hydroxide (NH_4OH)
5. Silver Standard Stock Solution; (1000 mg/liter): Dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$) analytical reagent grade, in deionized distilled water. Add 5 ml conc HNO_3 and bring to volume in a 500 ml volumetric flask. 1 ml = 1 mg Ag.
6. Iodine solution, IN: Dissolve 20 grams potassium iodide, (KI), analytical reagent grade, in 50 ml distilled deionized water. Add 12.7 grams iodine (I_2), analytical reagent grade, and dilute to 100 ml. Place in a brown bottle.

7. Cyanogen Iodide solution:

   To 50 ml deionized distilled water add 4.0 ml concentrated NH_4OH, 6.5 grams KCN, and 5.0 ml of Iodine solution prepared in 6). Mix and dilute to 100 ml with deionized distilled water. Do not keep longer than 2 weeks.

Procedure

Samples should be analyzed immediately after collection:

Sample Preparation

1. a. Transfer 100 ml of well-mixed sample to a 250 ml beaker. Add 3 ml conc HNO_3. Place the beaker on a hot plate and evaporate to near dryness, cautiously, in order to keep the sample from boiling. Cool, and add another 3 ml conc HNO_3. Cover the beaker with a watch glass and return to the hot plate. Heat so as to produce a gentle refluxing. Continue adding 3 ml portions of HNO_3 until the sample is light in color and no longer changes in color. Evaporate to near dryness and cool. Add 2 ml of 1:1 HNO_3 and warm the beaker just to dissolve the precipitates. Cool the liquid.

   b. If it is suspected that silver chloride has formed or silver has plated out, add about 80 ml distilled deionized water. Make the solution basic (pH above 7) by addition of ammonium hydroxide. Rinse the pH meter electrodes into the solution with distilled deionized water. Add 1 ml cyanogen iodide. Mix and allow to stand for 1 hour.

c. Transfer quantitatively to a 100 ml volumetric flask and bring to volume with distilled deionized water.

3. If there are particulates such as silicates remaining in the sample it must be centrifuged and only the supernatant aspirated.

4. Prepare working standards from stock solution. To bracket the optimum concentration range the following is suggested:

   a. Transfer 10 ml stock solution to a 100 ml volumetric flask and bring to volume with distilled deionized water containing 10 ml HNO_3/liter. Concentration: 100 mg/liter.

   Note: If, in the sample preparation, it was necessary to add cyanogen iodide to insure redissolving of precipitated silver, then the standards must be treated in the same manner. Do not add acidified water in step 4. a. Transfer 10 ml of stock solution to a small beaker. Add distilled deionized 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 distilled deionized water. Add 1 ml cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100 ml volumetric flask and bring to volume with distilled deionized water.

b. Transfer 0, 0.5, 1.0, 2.0, 3.0 and 4.0 ml from a. to separate 100 ml volumetric flasks. Bring to volume with distilled deionized water containing 10 ml HNO_3/liter. The concentrations of these working standards will be 0, 0.5, 1.0, 2.0, 3.0, and 4.0 mg Ag/liter.

Note: If a. was treated with cyanogen iodide these working standards must be brought to volume with distilled deionized water made basic with ammonium hydroxide and containing 10 ml cyanogen iodide/liter.

5. Standard Addition

a. Take the 2, 3, and 4 mg standards and pipet 5 ml from each into separate 10 ml volumetric flasks. Add to each 2 ml of the prepared sample. Bring to volume with distilled deionized water containing 10 ml HNO_3/liter.

b. Add 2 ml of prepared sample to a 10 ml volumetric flask. Bring to volume with distilled deionized water containing 10 ml HNO_3 per liter. This is the blank.

Note: For a sample treated with cyanogen iodide these standard additions are brought to volume with distilled deionized water made basic with ammonium hydroxide and containing 10 ml cyanogen iodide/liter.

Note: The absorbance from the blank b. will be 1/5 that produced by the prepared sample. The absorption from the spiked standards will be 1/2 that produced by the standards plus the contribution from 1/5 of the prepared

sample. Keeping these in mind the correct dilutions to produce optimum absorbance can be judged.

Instrument Operation

Wavelength: 328.1 nanometers

Optimum Concentration Range: 0.1-4 mg/liter

Lower Detection Limit: 0.01 mg/liter

Fuel: Acetylene

Oxidant: Air

Type of flame: oxidizing

A general outline for instrument operation is given in section 8.49. Follow the manufacturer's instructions for the model being used.

Quantification

The absorbances of spiked samples and blank vs. the concentrations are plotted according to the Method of Standard Additions as defined in section 8.49. The extrapolated value will be 1/5 the concentration of the original sample.

If the plot does not result in a straight line a nonlinear interference is present. This can sometimes be overcome by dilution, or addition of other reagents if there is some knowledge about the waste.

Records

It is recommended that recorder outputs chart be retained as a permanent record of the results and test conditions.

Method 8.55

CYANIDE

Scope and Application

The following procedure can be used to determine the concentration of inorganic cyanide in a waste or leachate.

Inorganic cyanide may be present as either a simple soluble salt (e.g., NaCN) or complex radical (e.g., $K_3(Fe(CN)_6)$). These metal complexes have varying tendencies to dissociate and form toxic hydrogen cyanide in the presence of acids. It is such soluble cyanides that this method will address.

This method shall not be used to determine the "reactive" cyanide content of wastes containing iron-cyanide complexes.

Summary

The waste is divided into two parts. One is chlorinated to destroy susceptible complexes. Each part is then distilled to remove interferences and analyzed for cyanide. The fraction amenable to chlorination is determined by the difference in values.

During the distillation, cyanide is converted to hydrogen cyanide vapor which is trapped in a scrubber containing sodium hydroxide solution. This solution is then titrated with standard silver nitrate.

Interferences

1. Sulfides interfere with the titration. They may be precipitated with cadmium.
2. Fatty acids form soaps under alkaline titration conditions and interfere. They may be extracted with a suitable solvent.
3. Oxidizing agents may decompose the cyanide. They may be treated with ascorbic acid.
4. Thiocyanate presence will interfere by distilling over in the procedure. This can be prevented by addition of magnesium chloride.
5. Aldehydes and ketones may convert cyanide to cyanohydrin under the acid distillation conditions.

Reagents

1. Calcium Hypochlorite solution: Dissolve 5 g of hypochlorite ($Ca(OCl)_2$) in 100 ml of distilled water.
2. Sodium Hydroxide solution (1.25N): Dissolve 50 g of sodium hydroxide (NaOH) in distilled water and dilute to 1 liter.
3. Ascorbic acid: crystals.
4. Potassium Iodide-starch paper.
5. Lead acetate paper
6. Cadmium carbonate (powdered)
7. Hexane
8. Acetic acid solution (1 + 9)

9. Concentrated H_2SO_4

10. Silver Nitrate Standard solution (0.0192N):

    Dry 5g $AgNO_3$ crystals to constant weight at 40°C. Weigh out 3.2647 grams and dissolve in distilled water. Dilute 1000ml. (1ml = 1mg CN)

11. Rhodanine Indicator solution:

    Dissolve 20mg p-dimethyl-amino-benzalrhodanine in 100ml acetone.

12. Magnesium Chloride solution:

    Weigh 510g $MgCl_2 \cdot 6H_2O$ into a 1 liter volumetric flask. Dissolve and bring to volume with distilled water.

Apparatus:

1. Microburet, 5.0 ml, for titration.

2. Flasks, condenser, and tubing are needed as shown in the diagram. The boiling flask should be of 1 liter size with inlet tube and provision for a condenser. The gas absorber may be a Fisher-Milligan scrubber. Assemble as shown in the diagram.

Procedure

1. Test and treat the sample as follows if it is known or suspected that interferences are present:

   a. Sulfides:

      If a drop of the distillate on lead acetate test paper indicates the presence of sulfides, treat 25 ml more of the sample than that required for the cyanide determination with powdered cadmium carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate, measure the sample to use for analysis. Avoid a large excess of cadmium and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. Sulfides should be removed prior to preservation with sodium hydroxide.

   b. Fatty acids:

      1. Acidify the sample with acetic acid (1 + 9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

2. Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with NaOH solution.

c. Oxidizing agents:

1. Test a drop of the sample with potassium iodide-starch test paper (KI-starch 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 sample volume.

2. Take two sample aliquots. To one 500 ml aliquot or a volume diluted to 500 ml, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide solution (1.25N).

Caution: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, this reaction should be performed in a hood.

For convenience, the sample may be agitated in a 1 liter beaker by means of a magnetic stirring device.

3. Test for residual chlorine with KI-starch paper 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.

4. 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 insure the presence of excess reducing agent.

   Both the chlorinated and unchlorinated aliquots are now separately distilled as follows:

5. Place 500 ml of sample, or an aliquot diluted to 500 ml in the 1 liter boiling flask. Add 50 ml of sodium hydroxide (1.25N) to the absorbing tube and dilute if necessary with distilled water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

6. Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

Caution: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to readjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

7. Slowly add 25 ml conc. sulfuric acid through the air inlet tube. Rinse the tube with distilled water and allow the air flow to mix the flask contents for 3 min. Pour 20ml of magnesium chloride solution into the air inlet and wash down with a stream of water.
8. Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. 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.
9. Drain the solution from the absorber into a 250 ml volumetric flask and bring up to volume with distilled water washings from the absorber tube.
10. Titration:
    a. Add the solution or an aliquot diluted to 250 ml to a 500 ml erlenmeyer flask. Add 10-12 drops Rhodanine indicator.

Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5 or 10 ml microburet

may be conveniently used to obtain precise titration.

b. Titrate a blank using distilled water.

Calculation:

a. $CN, mg/l = \frac{(A - B)1,000}{ml\ orig.\ sample} \times \frac{250}{ml\ of\ aliquot\ titrated}$

where:

A = volume of $AgNO_3$ for titration of sample.

B = volume of $AgNO_3$ for titration of blank.

b. Cyanide amenable to chlorination:

$CN, mg/l = A - B$

A = mg/l total cyanide in unchlorinated aliquot

B = mg/l total cyanide in chlorinated aliquot

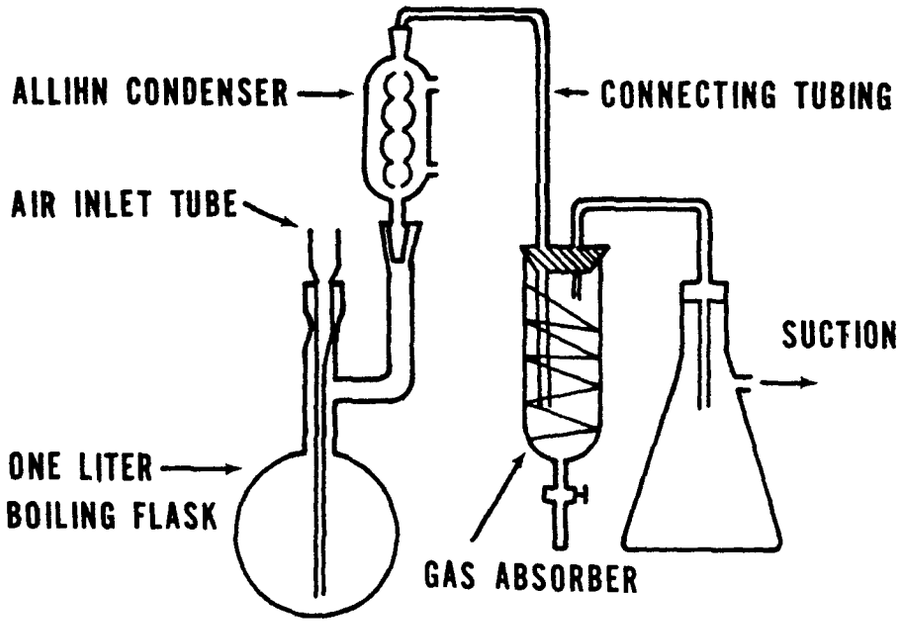


Figure 8.55-1
APPARATUS FOR CYANIDE DISTILLATION

METHOD 8.80

DIRECT INJECTION

Direct injection is the simplest and most precise technique for introducing a liquid into a measurement instrument since transfer losses are eliminated. Samples are introduced into the gas chromatograph by injection through the injection port, into the liquid chromatograph using either the injection port or sample loop, or into the atomic absorbtion spectrometer by aspiration into the flame or injection into the graphite furnace.

Direct injection should only be used with liquids free of particulate matter and in the case of the gas chromatograph also free of non-volatile species (e.g., lipids, polymers) in order to prevent column degradation.

When using direct injection of wastes caution must be exercised to prevent column or detector overload. To insure that valid results are obtained the analyst should initially conduct range finding experiments to insure that the sample matrix is free enough from interfering species so that the contaminant of interest can be determined if present in the sample at a levl of 1 ug/gm of sample level. If such sensitivity cannot be obtained, then additional sample cleanup (e.g., column chromatography, liquid-liquid extraction, exclusion chromatography) must first be carried out.

Method 8.56

TOTAL ORGANIC HALIDE

1. Scope and Application

   1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species 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.

   1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

   1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

   1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. 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 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 pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be 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 minutes. 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 help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which 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.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

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

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. 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.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 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^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID 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.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 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 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 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.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 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 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.

7.2.1 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.

7.3 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.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done 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.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 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.

9.3 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.

10. Pyrolysis Procedure

10.1 The contents of each column is 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.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 800°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, 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 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be 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-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses. the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 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.

13.3 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.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose µg/L	Dose as µg/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

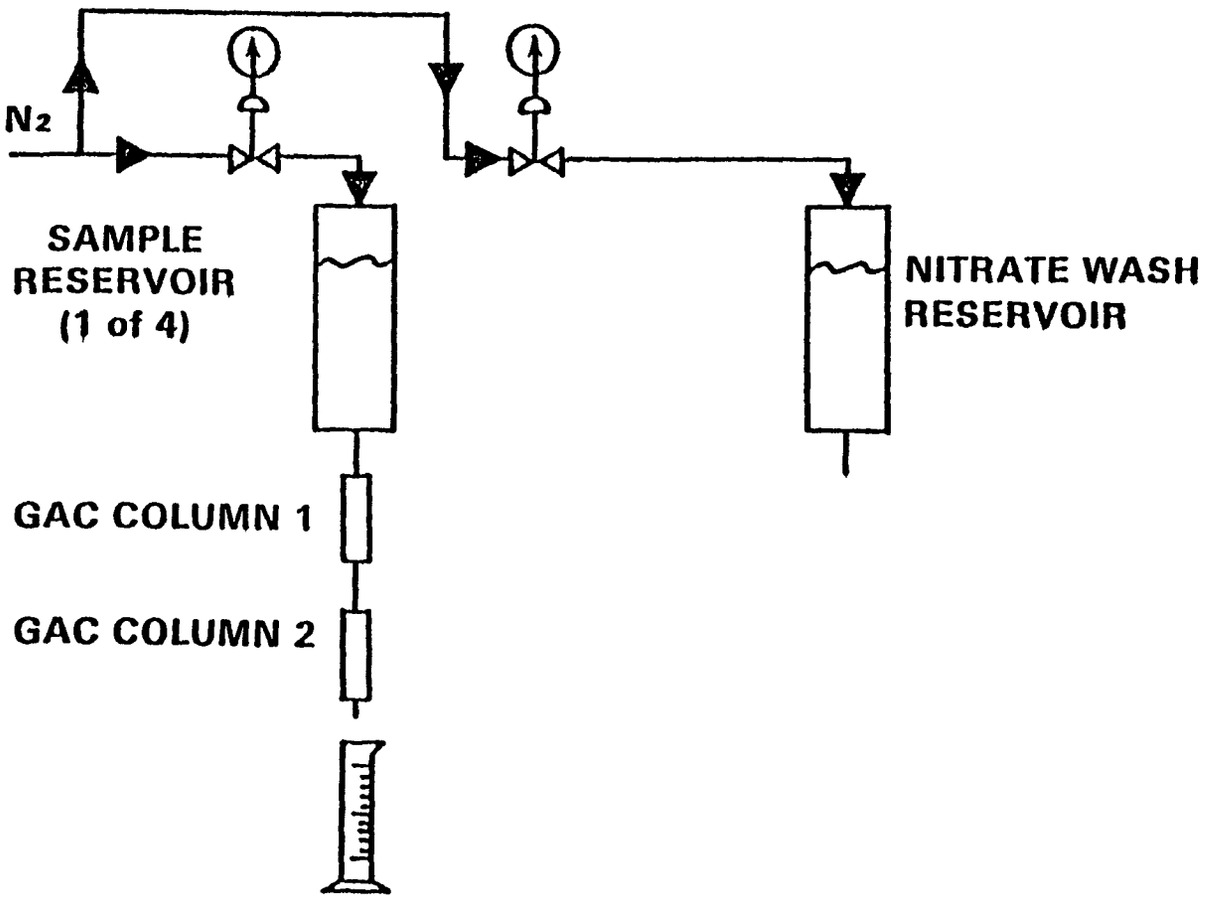


Figure 1. Adsorption Schematic

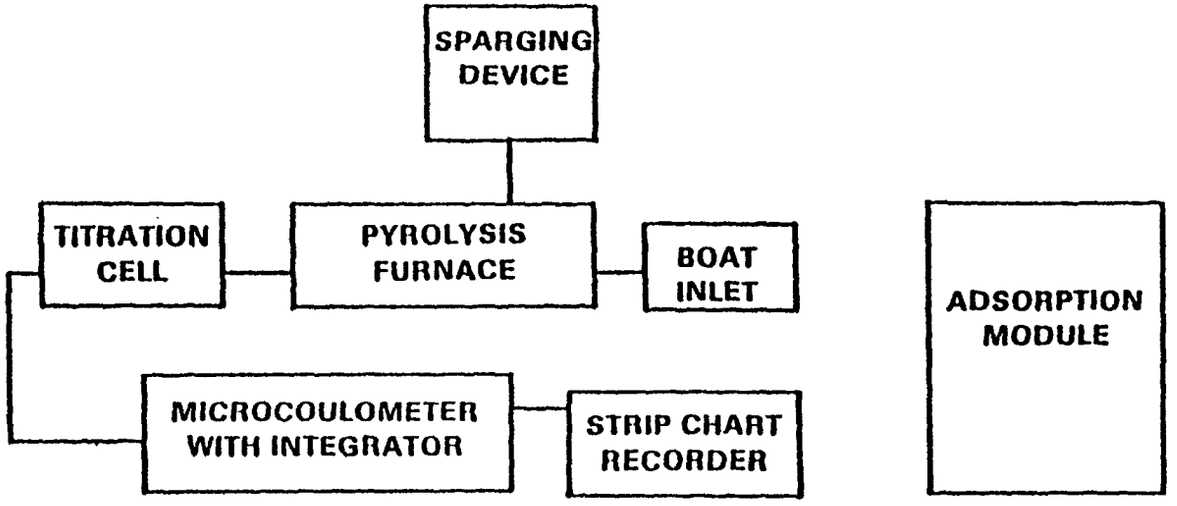


Figure 2. CAOX Analysis System Schematic

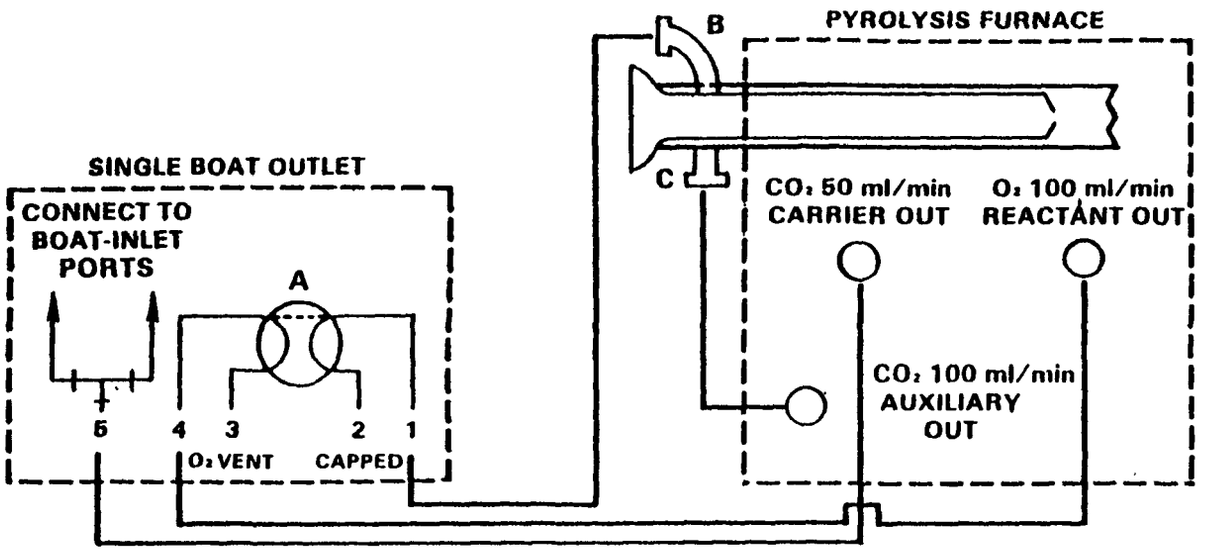


Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

Method 8.57

Sulfides

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/l
2. 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. Comments
   3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.
   3.2 Samples must be taken with a minimum of aeration. Sulfide may be volitilized by aeration and any ozygen inadvertently added to the sample may convert sulfide to an unmeasurable form.
   3.3 If the sample is not preserved with zinc acetate, the analysis must start immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.
4. Apparatus: Ordinary laboratory glassware
5. Reagents
   5.1 Hydrochloric acid, HCl, 6N
   5.2 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.
   5.3 Phenylarsine oxide 0.0250 N: commercially available.
   5.4 Starch indicator: commercially available.
   5.5 Procedure for standardization (see Residual Chlorine-iodometric titration)
6. Procedure
   6.1 Unprecipitated sample
      6.1.1 Place a known amount of standard iodine solution (5.2) into a 500 ml flask. The amount should be estimated to be in excess of the amount of sulfide expected.
      6.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.
      6.1.3 Add 2 ml of 6N HCl (5.1)
      6.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.
      6.1.5 If the iodine color disappears, add more iodine

until the color remains. Record the total number of milliliters of the standard iodine used in performing steps 6.1.1 and 6.1.5.

6.1.6 Titrate with reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution (5.3)) using the starch indicator (5.4) until the blue color disappears. Record the number of milliliters used.

6.2 Precipitated samples

6.2.1 Add the reagents to the sample in the original bottle. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3 Dewatered samples

6.3.1 Return the glass fibre filter paper which contains the sample to the original bottle. Add 200 ml of distilled water. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3.2 The calculations (7) should be based on the original sample put throug the filter.

7. Calculations

7.1 One ml of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.

7.2 Use the formula

mg/l sulfide = 400(A-B)/ml sample

where:

A=ml of 0.0250 N standard iodine solution (5.2)
B=ml of 0.0250 N standard reducing sodium thiosulfate or phenylarsine oxide solution (5.3)

8. Precision and Accuracy

8.1 Precision and accuracy for this method have not been determined.

*U.S. GOVERNMENT PRINTING OFFICE:1981 341-082/248 1-3

Method 8.82

HEADSPACE METHOD

Scope and Application

This method provides a procedure for the extraction of volatile organic compounds in pastes and solids. The static headspace technique is a simple method which 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 less than 125°C. Due to their low solubility, low molecular weight compounds can only be detected at high concentrations or at reduced pressure.

The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

Static Headspace Technique

Summary of Method

The waste 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.

Apparatus

1. Gas-tight syringe - 5-cc.
2. Head space standard solutions - Prepare two standard solutions of the compounds being determined at the 50-ng/ul and

250-ng/ul concentrations. Standard solutions should be prepared using methanol, methane, or other appropriate solvent. The standard solutions should be stored at less than 0°C, then allowed to warm to room temperature before dosing. Fresh standards should be prepared weekly. Procedures for preparing standards are outlined in the Purge and Trap Procedure of this manual (Method 8.83).

3. Vials, 125 ml "Hypo-Vials" (Pierce Chemical Co., #12995), or equivalent.
4. Septa, "Tuf-Bond" (Pierce #12720), or equivalent.
5. Seals, aluminum, (Pierce #13214), or equivalent.
6. Crimper, hand, (Pierce #13212), or equivalent.

Procedure

1. Place 10.0-g each of the well-mixed waste sample into five separate 125-ml septum seal vials.
2. Dose one sample vial through the septum with 200-ul of the 50-ng/ul standard methanol solution. Dose a second vial with 200-ul of the 250-ng/ul standard.
3. Place the two dosed sample vials and one non-dosed sample into a 90°C water bath for 1 hour. Store the two remaining samples near 4°C for possible future analyses.
4. While maintaining the sample at 90°C, withdraw 2.0-ml of the head 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. Analyze all three samples in exactly the same manner. Subtract the peak areas of compounds found in the undosed sample from the corresponding compounds contained in the dosed samples.

If a positive response is noted then the waste has not been demonstrated to be free of the contaminant of interest and is thus not fundamentally different than the listed waste. If no response is noted then the required sensitivity lug/gm sample) of the procedure must be confirmed using spiked samples.

Note: Standard quality assurance protocols should be employed, including blanks, duplicates, and dosed samples, as described in Section 10.

Bibliography

1. "Interim Methods for the Sampling and Analyses of Priority Pollutants in Sediments and Fish Tissue," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 [1980].

2. "Master Scheme for the Analysis of Organic Compounds in Water, Part I: State-of-the-Art Review of Analytical Operations," U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia 30605.

3. "An EPA Manual for Organic Analysis Using Gas Chromatography - Mass Spectrometry," W.L. Budde and J.W. Eichelberger, U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, Cincinnati, Ohio, 1979, EPA/600/8-79/006, Order Number PB-297164.

Method 8.83

PURGE AND TRAP METHOD

Scope and Application

This method covers a procedure for the extraction of purgeable organic compounds from aqueous liquids and free flowing paste samples prior to gas chromatographic analysis.

The success of the extraction depends on partitioning the compounds between the sample phase and gaseous headspace phases. This partitioning is a function of temperature, interfacial area, the volatility of the species being analyzed for, its solubility in the liquid being purged, and the volatility of the waste matrix. For highly volatile matrices, direct injection preceded by dilution, if necessary, should be used. For pastes, dilution of the sample until it becomes free flowing is used to insure 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.

Summary of Method

An inert gas is bubbled through the sample contained in a specially-designed purging chamber. This purging transfers the volatile compounds from the liquid phase to the vapor phase. The gaseous effluent is then swept through a short sorbent tube where the organic compounds are trapped. After purging is completed, the trap is heated and backflushed to

desorb the compounds into a gas chromatograph for subsequent identification and measurement.

Apparatus

1. Vial, with cap--40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.
2. Septum, Teflon faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.
3. Purge and Trap Device; The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (1). 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 absorbent as described in Table 8.83-1 (See Figures 8.83-1 through 8.83-4). 10-cm traps may be used providing that the recoveries are demonstrated to be comparable to the 25-cm traps.

Reagents

1. Trap Materials, see Table 8.83-1.
2. Activated carbon Filtrasorb 200 (Calgon Corp.) or equivalent
3. Organic-free water

Organic-free water is defined as water free of interferences when employed in the purge and trap procedure. It is generated by passing distilled or deionized water through a carbon filter bed containing activated carbon. A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling deionized distilled water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

Procedures

1. Assemble the purge and trap device (see Figures 8.83-1 through 8.83-4). Purge parameters to be used depend on the compounds being analyzed for; see Table 8.83-1. Pack the trap as shown in Figure 8.83-2 and condition overnight at a nominal 180°C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180°C.
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.
3. Adjust the purge gas (nitrogen or helium) flow rate according to Table 8.83-1.

4. 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.
5. 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 non-volatile solvent to the sample. In such cases diluting can be performed in the purging device.
6. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data.
7. Add 5.0 ml of the spiking solution through the valve bore, then close the valve.
8. 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 8.83-1. If method 8.02 will be used for analysis of the sample, dry the trap by maintaining a flow rate of 40 ml/minute dry purge for 6 minutes.

9. 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 8.83-1, while backflushing the trap with an inert carrier gas at 20 to 60 ml/minute for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45 or 50°C.

10. While the trap is being desorbed into the gas chromatograph, clean the purging chamber. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample. After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

    Note: If this bake out step is omitted when using GC/MS as the measurement technique, the amount of water entering the GC/MS system will progressively increase causing deterioration and potential shut down of the system.

11. 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.

References

1. "Determining Volatile Organics at Microgram-per-liter Levels by Gas Chromatography," T.A. Bellar and J.J. Lichtenberg, Journal. AWWA, 66, 739-744, Dec. 1974.

Table 8.83-1

PURGE AND TRAP PARAMETERS

Analysis Method*	8.01	8.02	8.03	8.24
Purge Gas	Nitrogen or Helium	Nitrogen or Helium	Helium	Nitrogen or Helium
Purge Gas Flow Rate (ml/min)	40	40	20 + 1	40
Purge Time (minutes)	11.0	12.0	30.0	12.0
Purge Temperature (°C)	180°	180°	170°	180°
Desorbtion Gas Flow Rate (ml/min)	20	20	20	20
Sorbants To Be Used in Packing Tube	A	B	C	D
		Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene Oxide).		
	A	Three percent OV-1 on Chromosorb-W, 60/80 mesh.		
		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.		
		Porous polymer packing, 60/80 mesh chromatographic grade Tenax GC (2,6-Diphenylene Oxide).		
	B	Three percent OV-1 on Chromosorb-W, 60/80 mesh.		
		Silica gel, 35-60 mesh, Davison grade-15 or equivalent.		
	C	Porous polymer packing, 50/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene Oxide).		

	Three percent OV-1 on Chromosorb-W, 60/80 mesh.
	Silica gel, 35-60 mesh, Davison grade-15 or equivalent.
	Porous polymer packing, 60/80 mesh, chromatographic grade Tenax GC (2,6-Diphenylene Oxide).
D	Three percent OV-1 on Chromosorb-W, 60/80 mesh.
	Silica gel, 35-60 mesh, Davison grade-15 or equivalent.

*Measurement method to be employed for identification and quantification

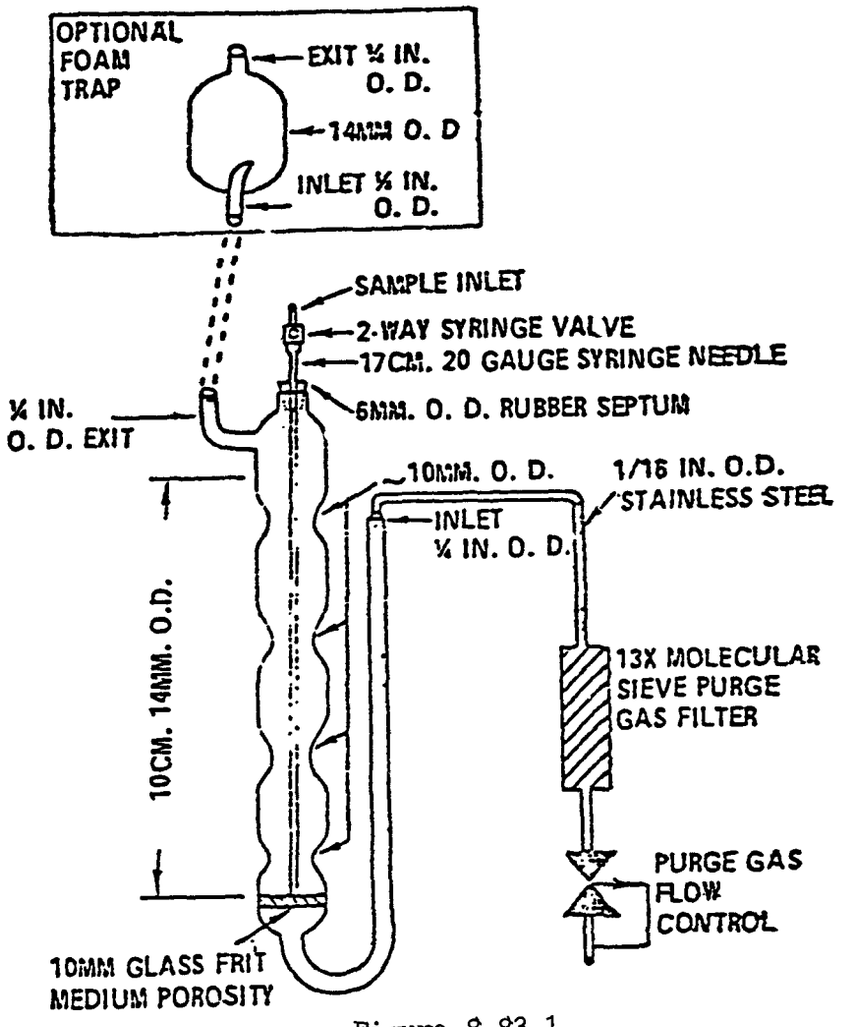


Figure 8.83-1
PURGING DEVICE

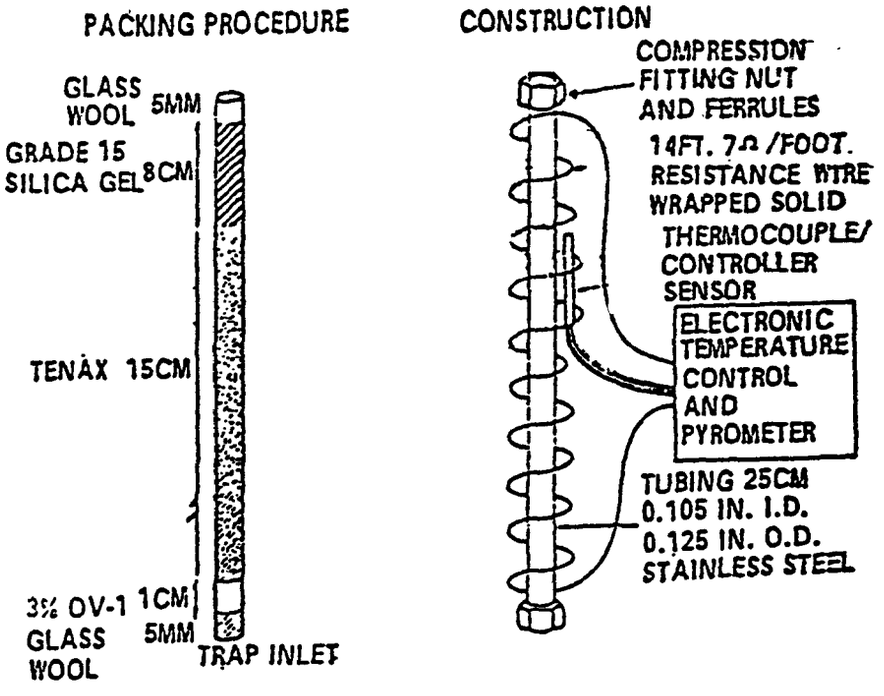


Figure 8.83-2
TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

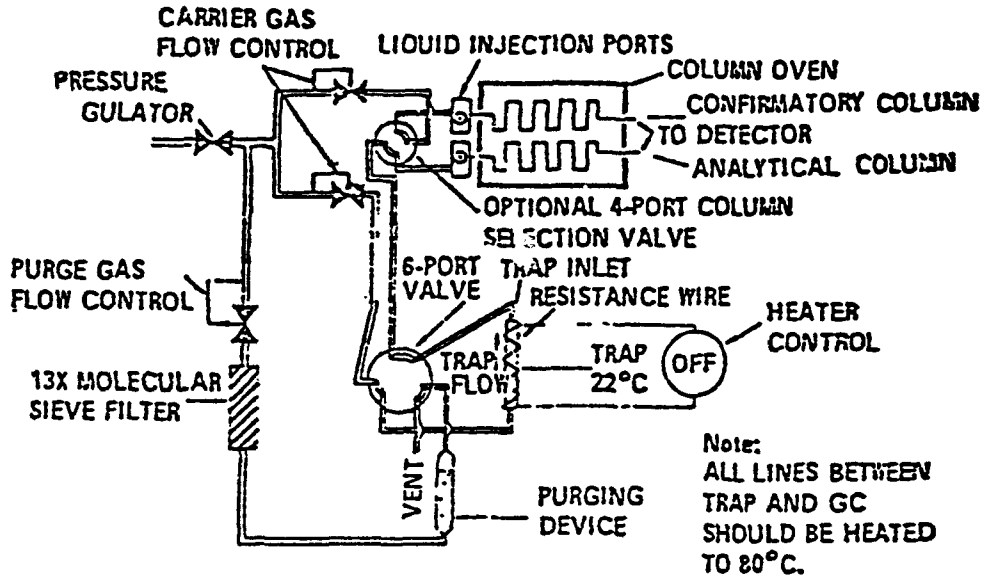


Figure 8.83-3
SCHEMATIC OF PURGE AND TRAP DEVICE-PURGE MODE

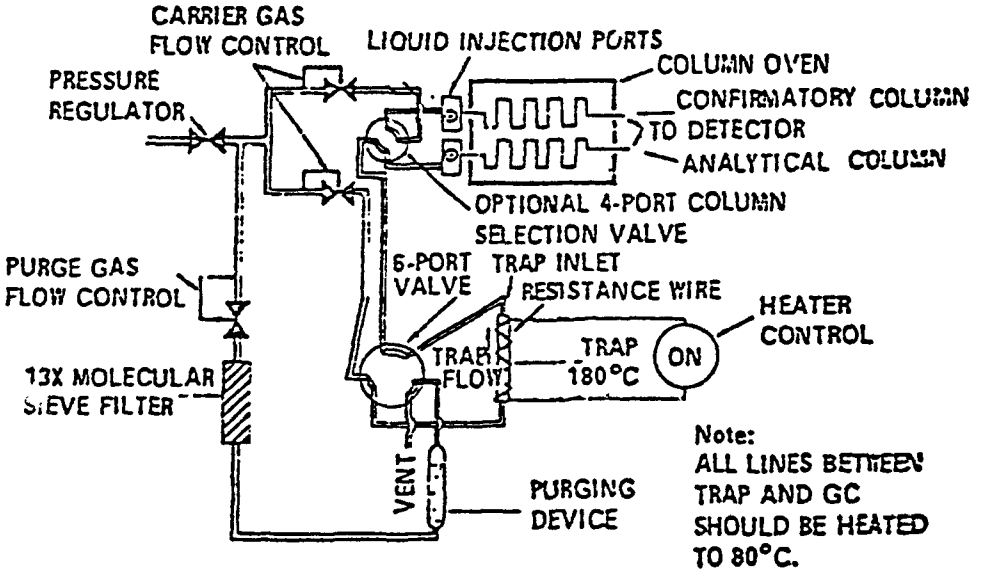


Figure 8.83-4
SCHEMATIC OF PURGE AND TRAP DEVICE DESORB MODE

Method 8.84

SHAKE OUT PROCEDURE

Introduction

This procedure provides a method for treating liquid wastes not soluble in the extraction solvent in order to extract the organic species prior to measurement by chromatography or, if necessary, further clean-up.

Summary of Method

Samples are made acid or alkaline, if necessary, then extracted three times, with the appropriate solvent using vigorous agitation. After the combined extracts are dried with anhydrous sodium sulfate, they are concentrated in a Kuderna-Danish Apparatus.

Apparatus

1. Separatory funnel - 250 ml, with Teflon stopcock.
2. Drying column - 20 mm ID Pyrex chromatographic column with coarse frit.
3. Kuderna-Danish (K-D) Apparatus. [Kontes K-570000 or equivalent.]
4. Boiling chips - solvent extracted, approximately 10/40 mesh.
5. Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm$ 2° C). The bath should be used in a hood.

Reagents

1. Sodium hydroxide, (ACS) 10 N in distilled water.

2. Sulfuric acid, (1+1), Mix equal volumes of concentrated H_2SO_4 (ACS) with distilled water.
3. Methylene chloride, acetone, 2-propanol, hexane, toluene-Pesticide quality or equivalent.
4. Sodium sulfate (ACS) Granular, anhydrous (purified by heating at 400° C for four hours in a shallow tray).

Procedure

1. Transfer 50 gms of sample to the separatory funnel.
2. Adjust the pH of the sample to that indicated in Table 8.84-1.
3. Add 50 ml of the appropriate extraction solvent (see Table 8.84-1).
4. Seal and shake the separatory funnel for 60 seconds with periodic venting to release vapor pressure.
5. Allow the phases to separate for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation.
6. Collect the extract and then repeat the extraction two more times using fresh portions of solvent.
7. Combine the three extracts and discard the now extracted waste.

8. Filter the extract and then dry it by passing it through a drying column containing 10 cm of anhydrous sodium sulfate.
9. Transfer the dried extract to the K-D apparatus. Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml extraction solvent to the top. Place the K-D apparatus on a hot water bath (60-65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.
10. Transfer to 10 ml volumetric flask and dilute to volume.

Table 8.84-1

EXTRACTION CONDITIONS

Compound	Extraction pH	Extraction Solvent
Acetonitrile	NA	NA
Acrolein	NA	NA
Acrylamide	NA	NA
Acrylonitrile	NA	NA
Benzene	NA	NA
Benzo(a)anthracene	5-9	Methylene Chloride
Benzo(a)pyrene	> 11	Methylene Chloride
Benzotrichloride	5-9 or > 11	Methylene Chloride
Benzyl chloride	5-9 or > 11	Methylene Chloride
Benzo(b)fluoranthene	5-9	Methylene Chloride
Bis(2-chloroethoxy-methane)	NA	NA
Bis(2-chloroethyl)ether	NA	NA
Bis(2-chloroisopropyl) ether	NA	NA
Carbon disulfide	NA	NA
Carbon tetrachloride	NA	NA
Chlordane	5-9 or >11	Methylene Chloride
Chlorinated dibenzo dioxins	6-8	Methylene Chloride
Chlorinated biphenyls	5-9 or >11	Methylene Chloride
Chloroacetaldehyde	NA	NA
Chlorobenzene	NA	NA

NA = Method not applicable to analysis for this compound.

EXTRACTION CONDITIONS cont. (2)

Compound	Extraction pH	Extraction Solvent
2-Chlorophenol	12	Methylene Chloride
Chrysene	5-9	Methylene Chloride
Creosote	5-9 or > 11	Methylene Chloride
Cresol(s)	12	Methylene Chloride
Cresylic acid(s)	12	Methylene Chloride
Dichlorobenzene(a)	5-9 or > 11	Methylene Chloride
Dichloroethane(s)	NA	NA
Dichloromethane	NA	NA
Dichlorophenoxy-acetic acid	> 7 or > 11	Ethyl Ether or Methylene Chloride
Dichloropropanol	5-9 or > 11	Methylene Chloride
2,4-Dimethylphenol	12	Methylene Chloride
Dinitrobenzene	5-9 or > 11	Methylene Chloride
4,6-Dinitro-O-cresol	12	Methylene Chloride
2,4-Dinitrotoluene	5-9 or > 11	Methylene Chloride
Endrin	5-9 or > 11	Methylene Chloride
Ethyl Ether	NA	NA
Formaldehyde	NA	NA
Formic Acid	5-9 or > 11	Methylene Chloride
Heptachlor	5-9 or > 11	Methylene Chloride
Hexachlorobenzene		
Hexachlorobutadiene	5-9 or > 11	Methylene Chloride
Hexachloroethane	5-9 or > 11	Methylene Chloride

EXTRACTION CONDITIONS cont. (3)

Compound	Extraction pH	Extraction Solvent
Hexachlorocyclo-pentadiene	5-9 or > 11	Methylene Chloride
Lindane	5-9 or > 11	Methylene Chloride
Maleic anhydride	5-9 or > 11	Methylene Chloride
Methanol	NA	NA
Methomyl	6.5 - 7.5	Methylene Chloride
Methyl ethyl ketone	> 11	Methylene Chloride
Methyl isobutyl ketone	> 11	Methylene Chloride
Naphthalene	5-9 or > 11	Methylene Chloride
Napthoquinone	5-9 or > 11	Methylene Chloride
Nitrobenzene	5-9	Methylene Chloride
4-Nitrophenol	12	Methylene Chloride
Paraldehyde (trimer of acetaldehyde	NA	NA
Pentachlorophenol	12	Methylene Chloride
Phenol	12	Methylene Chloride
Phorate	6-8	Methylene Chloride
Phosphorodithioic acid esters	5-9	Methylene Chloride
Phthalic anhydride	5-9 or > 11	Methylene Chloride
2-Picoline	5-9 or > 11	Methylene Chloride
Pyridine	5-9 or > 11	Methylene Chloride
Tetrachlorobenzene(s)	5-9 or > 11	Methylene Chloride
Tetrachloroethane(s)	NA	NA

EXTRACTION CONDITIONS cont. (4)

Compound	Extraction pH	Extraction Solvent
Tetrachloroethene	NA	NA
Tetrachlorophenol	12	Methylene Chloride
Toluene	NA	NA
Toluenediamine	> 11	Methylene Chloride
Toluene diisocyanate(s)	59	Methylene Chloride
Toxaphene	5-9 or > 11	Methylene Chloride
Trichloroethane	NA	NA
Trichloroethene(s)	NA	NA
Trichlorofluoromethane	NA	NA
Trichlorophenol(s)	12	Methylene Chloride
2,4,5-TP(Silvex)	<7 or > 11	Ethyl Ether or Methylene Chloride
Trichloropropane	NA	NA
Vinyl chloride	NA	NA
Vinylidene chloride	NA	NA
Xylene	NA	NA

Method 8.85

SONICATION METHOD

Scope and Application

This method covers a procedure for the extraction of non-volatile and semi-volatile organic compounds from solids. The sonication produces solid disruption to ensure intimate contact of the sample matrix with the extraction solvent.[1]

Summary of Method

A weighed sample of the solid waste is ground, mixed with the extraction medium, then dispersed into the solvent using sonication. The resulting solution may then be cleaned up further or analyzed directly using the appropriate technique (Methods 8.24 through 8.25).

Apparatus

1. Apparatus for Grinding.*†

   The necessity for grinding and the choice of grinding apparatus will depend on the physical and chemical characteristics of the solid waste material in question. Any of

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[1] The high energy vibrations produced by this method may produce artifacts and may drive off some semi-volatile compounds.

* Grinding is only necessary if the waste cannot either pass through a 1-mm standard seive or be extracted through a 1-mm diameter hole.

† Specific equipment listed in this method are for descriptive purposes only. Equivalent equipment is available from other manufactures and laboratory supply companies.

the following grinders, or their equivalent, would be suitable:

a. Fisher Mortar Model 155 Grinder or equivalent. Fisher Scientific Co., Catalogue Number 8-323. This grinder handles all except gummy, fibrous or oily materials.

Sonication

For purposes of solid waste dispersion, ultra-sonication must be performed by use of a horn-type sonicator. The following equipment or its equivalent is suitable.

a. Sonifer/Cell disruptor, model W-350, Ultrasonics Inc.

b. Sonic Dismembrator model 300, Fisher Scientific Co., Catalogue Number 15-338-40.

With either apparatus a sonicator probe with a titanium tip must be used.

Reagents

1. Any solvent appropriate for GC or GC/MS analysis. Choice of solvent will depend on the substances being analyzed for. The solvent of choice should be appropriate for the method of measurement to be used and which will give an analyte to solvent partition coefficient of at least 1 to 1000.
2. Sodium sulfate, (ACS) Granular anhydrous (purified by heating at 400° C for 4 hours in a shallow tray).

Procedure

1. Grind, or otherwise subdivide the waste, in a manner such that it either passes through a 1-mm seive or can be extruded through a 1-mm hole. Introduce sufficient sample

into the grinding apparatus to yield at least 10 gms after grinding.

2. Weigh 10.0 gm of suitably dispersed material into a 75 ml glass flask, add 30 ml of an appropriate solvent. Sonicate with agitation for approximately 15 minutes. 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 minutes. Solvent of choice should be one with properties which allow for efficient GC, LC, or GC/MS analysis, and which has an analyte to solvent partition coefficient on the order of 1 to 1000.
3. After the extraction is complete, filter the extract and dry it by passing it through a 4-inch 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 and a 3 ball Snyder column. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent. If the extract is expected to contain no interfering organics (therefore requiring no clean-up step), it may be concentrated using the K-D apparatus and analyzed by the appropriate gas or liquid chromatographic technique. If further clean-up is required proceed accordingly (see Section 9 of this manual) after concentration of the extract.

4. Heat the K-D apparatus on a steam bath until the liquid level in the collection tube is below 5 ml. Turn off the heat and allow K-D to cool. Transfer to 10 ml volumetric flask and adjust volume to 10 ml.

Method 8.86

SOXHLET EXTRACTION METHOD

Scope and Application

This method provides a procedure for the extraction of semi-volatile and nonvolatile organic compounds from waste materials which are in a "solid" state, prior to analysis by the appropriate gas chromatographic or liquid chromatographic technique.

Summary of Method

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. The extract is then concentrated, and may either be cleaned up further, or analyzed directly by the appropriate measurement technique (Methods 8.04 through 8.25).

Apparatus

1. Soxhlet extractor - 40 mm ID, with 500-ml round bottom flask.
2. Kuderna-Danish Apparatus [Kontes K-570000 or equivalent] with 3-ball Snyder column.
3. Chromatographic column--Pyrex, 20 mm ID, approximately 400 mm long, with coarse fritted plate on bottom and an appropriate packing medium.

Reagents

1. An appropriate solvent or solvent mixture yielding no measurable residue on evaporation.

2. Anhydrous granular sodium sulfate, ACS (purified by heating at 400° C for 4 hours in a shallow tray).

Procedure

1. Blend 10 grams of the solid sample with an equal weight of anhydrous sodium sulfate and place in either a glass or paper extraction thimble.
2. Place the sample in the extractor thimble. (If any problems are encountered in using the thimble, e.g., if the sample clogs the thimble, an alternative to the thimble would be to place a plug of glass wool in the extraction chamber, transfer the sample into the chamber, then cover the sample with another plug of glass wool.)
3. Place 300 ml of the solvent into a 500-ml roundbottom flask containing a boiling stone; attach the flask to the extractor, and extract the solids for 16 hours.
4. After the extraction is complete, cool the extract; then filter the extract and dry it by passing it through a 4-inch 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 10ml graduated concentrator tube. Wash the extractor flask and sodium sulfate column with 100-125 ml of the extracting solvent. If the extract is expected to contain no interfering organics (therefore requiring no clean-up step), it may be concentrated using the K-D apparatus and analyzed by the appropriate gas or liquid chromatographic technique. If further clean-up is required proceed accordingly (see Section 9 of this manual) after concentration of the extract.

5. Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml 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 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.
6. Transfer to 10 ml volumetric flask and adjust volume to 10 ml.

References

1. "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue", U.S. Environmental Protection Agency; Environmental Monitoring and Support Laboratory; Cincinnati, Ohio 45268.

2. "Recovery of Organic Compounds from Environmentally Contaminated Bottom Materials", T. Bellar, J. Lichtenberg, S. Lonneman; U.S. Environmental Protection Agency; Environmental Monitoring and Support Laboratory; Cincinnati, OH 45268.

Method 9.01

LIQUID - LIQUID EXTRACTION

Introduction

The following procedure provides a method of sample clean-up 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 interfering species.

Summary of Method

Removal of interferences is accomplished by a series of liquid-liquid extractions conducted at different pHs and with a variety of solvents.

Apparatus

1. Separatory funnel with Teflon stopcock.
2. Kuderna-Danish (K-D) Apparatus [Kontes-K-570000 or equivalent] equipped with a three ball Snyder column.
3. Boiling chips - solvent extracted, approximately 10/40 mesh.
4. Drying column - 20 mm I.D. Pyrex chromatographic column with coarse frit.
5. Water or steam bath.

Reagents

1. Sodium hydroxide-(ACS) 10 N in distilled water.
2. Sulfuric acid-(1 + 1) Mix equal volumes of concentrated H_2SO_4 (ACS) with distilled water.

3. Methylene chloride, acetone, 2-propanol, hexane, toluene-Pesticide quality or equivalent.
4. Sodium sulfate-(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).
5. Distilled Water

Procedure

1. Place 10 gms of the extract or organic liquid waste to be cleaned up into the separatory funnel.
2. Add 20 ml of the solvent indicated in Table 9.01-1.
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 one minute with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ 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 layer.
4. Separate the aqueous phase and transfer to a 125 ml Erlenmeyer flask.
5. Reextract the solvent layer twice more with 20 ml portions of distilled water at pH 12-13. Combine aqueous extract.
6. At this point the species being analyzed for will be in either the organic or aqueous phase (See Table 9.01-1). If in the aqueous phase discard the organic phase and proceed to

step 7. If in the organic phase discard the aqueous phase and proceed to step 12.

7. Transfer the aqueous phase to a clean separatory funnel.
8. Adjust the aqueous layer to a pH of 1-2 with sulfuric acid.
9. Add 20 ml of solvent to the funnel and shake for two minutes. Allow the solvent to separate from the aqueous phase and collect the solvent in a 100 ml Erlenmeyer flask.
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.
11. Perform a third extraction in the same manner.
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 quantitive transfer.
13. Add 1-2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml 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 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

14. If the appropriate analytical solvent is the same as that used for the above extraction then transfer extract to 10 ml volumetric flask and adjust volume to 10 ml. If a different solvent is to be used for sample measurement proceed as in step 15 where 2 propanol is used for illustrative purposes. Other solvents should be used as appropriate.

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 2-propanol. 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 2-propanol to the top. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 2.5 ml, remove the K-D apparatus and allow it to drain for at least 10

minutes while cooling. Add an additional 2 ml of 2-propanol through the top of the micro-Snyder column and resume concentrating as before. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. 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.

Table 9.01-1

APPROPRIATE CLEAN-UP SOLVENT AND STEP 6 PHASE

Compound Being Analyzed For	Solvent	Step 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	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

Table 9.01-1 (cont.)

APPROPRIATE CLEAN-UP SOLVENT AND STEP 6 PHASE

Compound Being Analyzed For	Solvent	Step 6 Phase
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
Napthalene	Dichloromethane	Solvent
Napthoquinone	Dichloromethane	Solvent
Nitrobenzene	Dichloromethane	Solvent
4-Nitrophenol	Dichloromethane	Aqueous
Pentachlorophenol	Dichloromethane	Aqueous
Phenol	Dichloromethane	Aqueous
Phorate	Dichloromethane	Aqueous
Phosphorodithioic acid esters	Dichloromethane	Solvent
Phthalic anhydride	Dichloromethane	Solvent
2-Picoline	Dichloromethane	Solvent

Table 9.01-1 (cont.)

APPROPRIATE CLEAN-UP SOLVENT AND STEP 6 PHASE

Compound Being Analyzed For	Solvent	Step 6 Phase
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

Section 10.0

QUALITY CONTROL, QUALITY ASSURANCE

INTRODUCTION

The procedures and methods that make up the body of this manual outline how to test for hazardous characteristics in solid wastes. If performed by qualified analysts the Agency feels that the procedures and methods will give a true verdict of the wastes being tested.

Yet, the described techniques are only valuable if they are performed with proper care. Unless the stated criteria of the quality controls and assurances called for in every technique are met the derived data will be of little value to either the Agency or the generator.

Section 10 is meant to give guidance to qualified analysts who will be testing solid wastes for hazardous characteristics. Since it was developed for use in the testing of dilute aqueous samples, it is not to be followed exactly. Rather it should be used as a guideline that outlines acceptable quality control procedures.

In the hands of a qualified analyst Section 10 can be used as a yardstick to compare the acceptability of data derived by generators of solid wastes. In future editions of this manual EPA will provide more specific quality assurance and control criteria for use in solid waste testing programs.

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HANDBOOK FOR ANALYTICAL QUALITY CONTROL IN WATER AND WASTEWATER LABORATORIES

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ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
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DISCLAIMER

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ABSTRACT

One of the fundamental responsibilities of water and wastewater management is the establishment of continuing programs to insure the reliability and validity of analytical laboratory and field data gathered in water treatment and wastewater pollution control activities.

This handbook is addressed to laboratory directors, leaders of field investigations, and other personnel who bear responsibility for water and wastewater data. Subject matter of the handbook is concerned primarily with quality control (QC) for chemical and biological tests and measurements. Chapters are also included on QC aspects of sampling, microbiology, biology, radiochemistry, and safety as they relate to water and wastewater pollution control. Sufficient information is offered to allow the reader to inaugurate or reinforce programs of analytical QC that emphasize early recognition, prevention, and correction of factors leading to breakdowns in the validity of water and wastewater pollution control data.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

Chapter 1

IMPORTANCE OF QUALITY CONTROL

1.1 General

The analytical laboratory provides qualitative and quantitative data for use in decision-making. To be valuable, the data must accurately describe the characteristics and concentrations of constituents in the samples submitted to the laboratory. In many cases, because they lead to faulty interpretations, approximate or incorrect results are worse than no result at all.

Ambient water quality standards for pH, dissolved oxygen, heavy metals, and pesticides are set to establish satisfactory conditions for drinking water, fishing, irrigation, power generation, or other water uses. The laboratory data define whether conditions are being met and whether the water can be used for its intended purposes. In wastewater analyses, the laboratory data identify the characteristics of the treatment plant influent and the final load imposed upon receiving water resources, as well as the effectiveness of steps in the treatment process. Decisions on process changes, plant modifications, or the construction of new facilities may be based upon the results of water laboratory analyses. The financial implications of such decisions suggest that extreme care be taken in analysis.

Effective research in water pollution control also depends upon a valid laboratory data base, which in turn may contribute to sound evaluations of both the progress of the research itself and the viability of available water pollution-control alternatives.

The analytical data from water and wastewater laboratories may also be used to determine the extent of compliance of a polluting industry with discharge or surface water standards. If the laboratory results indicate a violation of a standard, remedial action is required by the responsible parties. Both legal and social pressures can be brought to bear to protect the environment. The analyst should realize not only that he has considerable responsibility for providing reliable laboratory descriptions of the samples at issue, but also that his professional competence, the validity of the procedures used, and the resulting values reported may be challenged (perhaps in court). For the analyst to meet such challenges, he should support the laboratory data with an adequate documentation program that provides valid records of the control measures applied to all factors bearing on the final results of investigations.

1.2 Quality Assurance Programs

Because of the importance of laboratory analyses in determining practical courses of action that may be followed, quality assurance programs to insure the reliability of the water and wastewater data are essential. Although all analysts practice quality control (QC) in amounts depending upon their training, professional pride, and the importance of their particular projects, under actual working conditions sufficiently detailed QC may be neglected. An established, routine, quality assurance program applied to each analytical test can relieve analysts of the necessity of originating individual QC efforts.

Quality assurance programs have two primary functions in the laboratory. First, the programs should continually monitor the reliability (accuracy and precision) of the results reported; i.e., they should continually provide answers to the question "How good (accurate and precise) are the results obtained?" This function is the *determination* of quality. The second function is the *control* of quality (to meet the program requirements for reliability). As an example of the distinction between the two functions, the processing of spiked samples may be a determination of measurement quality, but the use of analytical grade reagents is a control measure.

Each analytical method has a rigid protocol. Similarly, QC associated with a test must include definite required steps for monitoring the test and insuring that its results are correct. The steps in QC vary with the type of analysis. For example, in a titration, standardization of the titrant on a frequent basis is an element of QC. In any instrumental method, calibration and checking out of instrumental response are also QC functions. All of the experimental variables that affect the final results should be considered, evaluated, and controlled.

In summary, laboratory data, in quantitative terms, e.g., in milligrams per liter, are reported by the analyst. These values are interpreted by industrial plant engineers to show compliance or noncompliance with permits for discharge, by state pollution control agencies to define the need for additional sampling and analysis to confirm violations, or by EPA to demonstrate that prescribed waste treatment was sufficient to protect the surface waters affected by the discharge.

This handbook discusses the basic factors of water and wastewater measurements that determine the value of analytical results and provides recommendations for the control of these factors to insure that analytical results are the best possible. Quality assurance programs initiated from, and based upon, these recommendations should increase confidence in the reliability of the reported analytical results.

Because ultimately a laboratory director must assume full responsibility for the reliability of the analytical results submitted, the laboratory director must also assume full responsibility in both design and implementation for the corresponding quality assurance program.

1.3 Analytical Methods

Many analytical methods for common water pollutants have been in use for many years and are used in most environmental laboratories. Examples are tests for chloride, nitrate, pH, specific conductance, and dissolved oxygen. Widespread use of an analytical method in water and wastewater testing usually indicates that the method is reliable, and therefore tends to support the validity of the reported test results. Conversely, the use of little-known analytical techniques forces the water and wastewater data user to rely on the judgment of the laboratory analyst, who must then defend his choice of analytical technique as well as his conclusions. Present Federal regulations, notably section 304(h) of Public Law 92-500 (Federal Water Pollution Control Amendments of 1977) and the Interim Drinking Water Regulations specifically require the use of EPA-approved methods of analysis.

Uniformity of methodology within a single laboratory as well as among a group of cooperating laboratories is required to remove methodology as a variable when there are many data users. Uniformity of methodology is particularly important when several

laboratories provide data to a common data bank (such as STORET*) or cooperate in joint field surveys. A lack of uniformity of methodology may raise doubts as to the validity of the reported results. If the same constituents are measured by different analytical procedures within a single laboratory, or by a different procedure in different laboratories, it may be asked which procedure is superior, why the superior method is not used throughout, and what effects the various methods and procedures have on the data values and their interpretations.

Physical and chemical measurement methods used in water or wastewater laboratories should be selected by the following criteria:

a. The selected methods should measure desired constituents of water samples in the presence of normal interferences with sufficient precision and accuracy to meet the water data needs.

b. The selected procedures should use equipment and skills ordinarily available in the average water pollution control laboratory or water supply laboratory.

c. The selected methods should be sufficiently tested to have established their validity.

d. The selected methods should be sufficiently rapid to permit repetitive routine use in the examination of large numbers of water samples.

The restriction to the use of EPA methods in all laboratories providing data to EPA permits the combination of data from different EPA programs and supports the validity of decisions made by EPA.

Regardless of which analytical methods are used in a laboratory, the methodology should be carefully documented. In some reports it is stated that a standard method from an authoritative reference (such as ref. 1) was used throughout an investigation, when close examination has indicated, however, that this was not strictly true. Standard methods may be modified or entirely replaced because of recent advances in the state of the art or personal preferences of the laboratory staff. Documentation of measurement procedures used in arriving at laboratory data should be clear, honest, and adequately referenced; and the procedures should be applied exactly as documented.

Reviewers can apply the associated precision and accuracy of each specific method when interpreting the laboratory results. If the accuracy and precision of the analytical methodology are unknown or uncertain, the data user may have to establish the reliability of the result he or she is interpreting before proceeding with the interpretation.

The necessarily strict adherence to accepted methods in water and wastewater analyses should not stifle investigations leading to improvements in analytical procedures. Even with accepted and documented procedures, occasions arise when the procedures must be modified; e.g., to eliminate unusual interferences, or to yield increased sensitivities. When a

*STORET is the acronym used to identify the computer-oriented U.S. Environmental Protection Agency water quality control information system; STORET stands for STOrage and RETrieval of data and information.

modification of a procedure is necessary, it should be carefully formulated. Data should then be assembled using both the original and the modified procedures to show the superiority of the latter. Such results can be brought to the attention of the organizations responsible for standardization of procedures. To increase the benefit, the modified procedures should be written in a standard format for routine use as applicable. The standard format usually includes scope and application, principle, equipment, reagents, procedure, calculation of results, and expected precision and accuracy.

Responsibility for the results obtained from use of a nonstandard procedure (i.e., one that has not become accepted through wide use) rests with the analyst and his supervisor.

In field operations, because it may be difficult to transport samples to the laboratory, or to examine large numbers of samples (e.g., for gross characteristics), the use of rapid field methods yielding approximate answers is sometimes required. Such methods should be used only with a clear understanding that the results obtained are not as reliable as those obtained from standard laboratory procedures. The fact that such methods have been used should be documented, and the results should not be reported in the same context with more reliable analytical information. When only approximate values are available, perhaps obtained for screening purposes in the field only, the data user would then be so informed.

1.4 Reference

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, American Public Health Association, New York (1975).

Chapter 2

LABORATORY SERVICES

2.1 General

Quality control of water and wastewater laboratory analyses involves consideration and control of the many variables that affect the production of reliable data. The quality of the laboratory services available to the analyst must be included among these variables. An abundant supply of distilled water, free from interferences and other undesirable contaminants, is an absolute necessity. An adequate source of clean, dry, compressed air is needed. Electrical power for routine laboratory use and voltage-regulated sources for delicate electronic instrumentation must be provided. This chapter, therefore, will be devoted to describing methods of maintaining the quality of these services, as used in water and wastewater laboratory operations.

2.2 Distilled Water

Distilled or demineralized water is used in the laboratory for dilution, preparation of reagent solutions, and final rinsing of glassware. Ordinary distilled water is usually not pure. It may be contaminated by dissolved gases and by materials leached from the container in which it has been stored. Volatile organics distilled over from the feed water may be present, and nonvolatile impurities may occasionally be carried over by the steam, in the form of a spray. The concentration of these contaminants is usually quite small, and distilled water is used for many analyses without further purification. However, it is highly important that the still, storage tank, and any associated piping be carefully selected, installed, and maintained in such a way as to insure minimum contamination.

Water purity has been defined in many different ways, but one generally accepted definition states that high-purity water is water that has been distilled or deionized, or both, so that it will have a specific resistance of 500,000 Ω or greater (or a conductivity less than 2.0 μmho/cm). This definition is satisfactory as a base to work from, but for more critical requirements, the breakdown shown in table 2-1 has been suggested to express degrees of purity (1).

Table 2-1
WATER PURITY

Degree of Purity	Maximum Conductivity (μmho/cm)	Approximate Concentration of Electrolyte (mg/l)
Pure	10	2-5
Very Pure	1	0.2-0.5
Ultrapure	0.1	0.01-0.02
Theoretically Pure	0.055	0.00

The American Society for Testing and Materials (ASTM) specifies four different grades of water for use in methods of chemical analysis and physical testing. The method of preparation of the various grades of reagent water determines the limits of impurities. The various types of reagent water and ASTM requirements are listed in table 2-2.

Type I grade water is prepared by the distillation of feed water having a maximum conductivity of 20 μmho/cm at 25°C followed by polishing with a mixed bed of ion-exchange materials and a 0.2-μm membrane filter.

Type II grade water is prepared by using a still designed to produce a distillate having a conductivity of less than 1.0 μmho/cm at 25°C. This may be accomplished by double distillation or the use of a still incorporating special baffling and degassing features.

Type III grade water is prepared by distillation, ion exchange, or reverse osmosis, followed by polishing with the 0.45-μm membrane filter.

Type IV grade water is prepared by distillation, ion exchange, reverse osmosis, or electrodialysis.

Properly designed metal stills from reputable manufacturers offer convenient and reliable sources of distilled water. These stills are usually constructed of copper, brass, and bronze. All surfaces that contact the distillate should be heavily coated with pure tin to prevent metallic contamination. The metal storage tank should be of sturdy construction with a tight-fitting cover, and have a filter in the air vent to remove airborne dust, gases, and fumes.

For special purposes, an all-glass distillation unit may be preferable to the metal still. These stills are usually smaller, and of more limited capacity than the metal stills. An actual comparison in which the distillates from an all-glass still and a metal still were analyzed spectrographically for certain trace metal contaminants is given in table 2-3. It can be seen that the all-glass still produced a product that had substantially lower contamination from zinc, copper, and lead.

All stills require periodic cleaning to remove solids that have been deposited from the feed water. Hard water and high-dissolved-solids content promote scale formation in the

Table 2-2
REQUIREMENTS FOR REAGENT WATER

Grade of Water	Maximum Total Matter (mg/l)	Maximum Electrical Conductivity at 25°C (μmho/cm)	Minimum Electrical Resistivity* at 25°C (MΩ · cm)	pH at 25°C	Minimum Color Retention Time of $KMnO_4$ (min)
Type I	0.1	0.06	16.67	–	60
Type II	0.1	1.0	1.0	–	60
Type III	1.0	1.0	1.0	6.2-7.5	10
Type IV	2.0	5.0	0.2	5.0-8.0	10

*See reference 2.

Table 2-3
COMPARISON OF DISTILLATES FROM GLASS AND METAL STILLS

Source	Element and Concentration (μg/l)							
	Zn	B	Fe	Mn	Al	Cu	Ni	Pb
All-Glass Still	<1	12	1	<1	<5	5	<2	<2
Metal Still	9	13	2	<1	<5	11	<2	26

evaporator, and cleaning frequency will thus depend on the quality of the feed water. The boiler of an all-glass still should be drained daily and refilled with clean water. Buildup of scale is easily detected, and the boiler and condenser coils should be cleaned at frequent intervals. Metal stills usually incorporate a constant bleeder device that retards scale formation to some extent. Nevertheless, these units should be dismantled and cleaned at regular intervals. Cleaning should always be in accordance with the manufacturer's instructions.

Pretreatment of the incoming feed water will often improve still performance and raise the quality of the distillate. For example, preliminary softening of hard water removes calcium and magnesium prior to distillation. This reduces scale formation in the boiler and condenser, thereby reducing maintenance service. These softeners employ the ion-exchange principle using a sodium chloride cycle, and are relatively inexpensive to operate. A carbon filtration system, installed at the feed-water intake, will remove organic materials that might subsequently be carried over in the distillate. If trace concentrations of ions are a major concern, the distillate may be passed through a mixed-bed ion exchanger.

At least two commercially manufactured systems are available for production of high-purity water by ion exchange. The Millipore Super-Q System (Millipore Corp., Bedford, Mass.) consists essentially of disposable cartridges for prefiltration, organic absorption, deionization, and Millipore filtration. The company claims it can produce 10-MΩ water, containing no particulate matter larger than 0.45 μm in size, from tap water, at the rate of 20 gal/h. Continental Water Conditioning Corp., El Paso, Tex., advertises a system that can be tailored to the needs of the customer. Performance specifications include minimum flow rates of 45 gal/h and total dissolved solids of less than 0.1 mg/l when required.

Specific conductance is a rapid and simple measurement for determining the inorganic quality of distilled water. Stills of the types previously discussed are capable of producing a distillate with a specific conductance of less than 2.0 μmho/cm at 25°C. This is equivalent to 0.5 to 1.0 mg/l of ionized material. Frequent checks should be made to determine that optimum performance is being maintained. A purity meter installed between the still and the storage reservoir will monitor the conductivity of the distillate, in terms of the equivalent in milligrams per liter of sodium chloride. If the reading on the meter begins to rise above the present limit of conductivity, effective action should be taken to eliminate the source of contamination. Organic quality is more difficult to monitor, but the total organic carbon determination is a simple and rapid test of organic contaminants.

A piping system for delivering distilled water to the area of use within the laboratory is a convenient feature. In this case, special care should be taken that the quality of the water is not degraded between the still and the point of use. Piping may be of tin, tin-lined brass, stainless steel, plastic, or chemically resistant glass, depending on the quality of the water desired, its intended use, and on available funds. Tin is best, but is also very expensive. As a compromise, plastic pipe or glass pipe with Teflon* O-rings at all connecting joints is satisfactory for most purposes. The glass pipe has an obvious advantage when freedom from trace amounts of organic materials is important.

When there is no piped-in supply, distilled water will probably be transported to the laboratory and stored in polyethylene or glass bottles of about 5-gal capacity. If stored in glass containers, distilled water will gradually leach the more soluble materials from the glass and cause an increase in dissolved solids. On the other hand, polyethylene bottles contain organic plasticizers, and traces of these materials may be leached from the container walls. These are of little consequence, except in some organic analyses. Rubber stoppers often used in storage containers contain leachable materials, including significant quantities of zinc. This is usually no problem, because the water is not in direct contact with the stopper. However, the analyst should be aware of the potential for contamination, especially when the supply is not replenished by frequent use.

The delivery tube may consist of a piece of glass tubing that extends almost to the bottom of the bottle, and that is bent downward above the bottle neck, with a 3- to 4-ft piece of flexible tubing attached for mobility. Vinyl tubing is preferable to latex rubber, because it is less leachable; however, a short piece of latex tubing may be required at the outlet for better control of the pinchcock. The vent tube in the stopper should be protected against the entrance of dust.

Ordinary distilled water is quite adequate for many analyses, including the determination of major cations and anions. Certain needs may require the use of double- or even triple-distilled water. Redistillation from an alkaline permanganate solution can be used to obtain a water with low organic background. When determining trace organics by solvent extraction and gas chromatography, distilled water with sufficiently low background may be extremely difficult to obtain. In this case, preextraction of the water with the solvent used in the respective analysis may be helpful in eliminating undesirable peaks in the blank. Certain analyses require special treatment or conditioning of the distilled water, and these will now be discussed.

2.2.1 Ammonia-Free Water

Removal of ammonia can be accomplished by shaking ordinary distilled water with a strong cation exchanger, or by passing distilled water through a column of such material. For limited volumes of ammonia-free water, use of the Quikpure (Box 254, Chicago, Ill.) 500-ml bottle is highly recommended. The ion-free water described in section 2.2.3 is also suitable for use in the determination of ammonia.

2.2.2 Carbon-Dioxide-Free Water

Carbon-dioxide-free water may be prepared by boiling distilled water for 15 min and cooling to room temperature. As an alternative, distilled water may be vigorously aerated with a

*Trademark of E. I. duPont de Nemours & Co.

stream of inert gas for a period sufficient to achieve saturation and CO_2 removal. Nitrogen is most frequently used. The final pH of the water should lie between 6.2 and 7.2. It is not advisable to store CO_2-free water for extended periods.

2.2.3 Ion-Free Water

A multipurpose high purity water, free from trace amounts of the common ions, may be conveniently prepared by slowly passing distilled water through an ion-exchange column containing one part of a strongly acidic cation-exchange resin in the hydroxyl form. Resins of a quality suitable for analytical work must be used. Ion-exchange cartridges of the research grade, available from scientific supply houses, have been found satisfactory. By using a fresh column and high-quality distilled water, a water corresponding to the ASTM designation for type I reagent water (2) (maximum 0.1 mg/l of total matter and maximum conductivity of 0.06 mho/cm) can be obtained. This water is suitable for use in the determination of ammonia, trace metals, and low concentrations of most cations and anions. It is not suited to some organic analyses, however, because this treatment adds organic contaminants to the water by contact with the ion-exchange materials.

2.3 Compressed Air

The quality of compressed air required in the laboratory is usually very high, and special attention should be given to producing and maintaining clean air until it reaches the outlet. Oil, water, and dirt are undesirable contaminants in compressed air, and it is important to install equipment that generates dry, oil-free air. When pressures of less than 50 psi are required, a rotary-type compressor, using a water seal and no oil, eliminates any addition of oil that would subsequently have to be removed from the system. Large, horizontal, water-cooled compressors will usually be used when higher pressures are required.

Compression heats air, thus increasing its tendency to retain moisture. An aftercooler is therefore necessary to remove water. Absorption filters should be used at the compressor to prevent moisture from entering the piping system. Galvanized steel pipe with threaded, malleable-iron fittings, or solder-joint copper tubing should be used for piping the air to the laboratory.

When the compressed air entering the laboratory is of low quality, an efficient filter should be installed between the outlet and the point of use to trap oil, moisture, and other contaminants. As an alternative, high-quality compressed air of the dry grade is commercially available in cylinders when no other source exists.

2.4 Vacuum

A source of vacuum in the chemical laboratory, while not an absolute necessity, can be a most useful item. While used primarily as an aid in filtration, it is also sometimes used in pipetting and in speeding up the drying of pipets.

2.5 Hood System

An efficient hood system is a requirement for all laboratories. In addition to removing the various toxic and hazardous fumes that may be generated when using organic solvents, or that may be formed during an acid digestion step, a hood system may also be used to remove toxic gases that may be formed during atomic absorption analyses or other

reactions. A regular fume hood should have a face velocity of 100 ft/min (linear) with the sash fully open.

2.6 Electrical Services

An adequate electrical system is indispensable to the modern laboratory. This involves having both 115- and 230-V sources in sufficient capacity for the type of work that must be done. Requirements for satisfactory lighting, proper functioning of sensitive instruments, and operation of high-current devices must be considered. Any specialized equipment may present unusual demands on the electrical supply.

Because of the special type of work, requirements for a laboratory lighting system are quite different from those in other areas. Accurate readings of glassware graduations, balance verniers, and other measuring lines must be made. Titration endpoints, sometimes involving subtle changes in color or shading, must be observed. Levels of illumination, brightness, glare, and location of light sources should be controlled to facilitate ease in making these measurements and to provide maximum comfort for the employees.

Such instruments as spectrophotometers, flame photometers, atomic absorption equipment, emission spectrographs, and gas chromatographs have complicated electronic circuits that require relatively constant voltage to maintain stable, drift-free instrument operation. If the voltage of these circuits varies, there is a resulting change in resistance, temperature, current, efficiency, light output, and component life. These characteristics are interrelated, and one cannot be changed without affecting the others. Voltage regulation is therefore necessary to eliminate these conditions.

Many instruments have built-in voltage regulators that perform this function satisfactorily. In the absence of these, a small, portable, constant-voltage transformer should be placed in the circuit between the electrical outlet and the instrument. Such units are available from Sola Basic Industries, Elk Grove Village, Ill., and are capable of supplying a constant output of 118 V from an input that varies between 95 and 130 V. When requirements are more stringent, special transformer-regulated circuits can be used to supply constant voltage. Only the instrument receiving the regulated voltage should be operated from such a circuit at any given time. These lines are in addition to, and separate from, the ordinary circuits used for operation of equipment with less critical requirements.

Electrical heating devices provide desirable heat sources, and should offer continuously variable temperature control. Hot plates and muffle furnaces wired for 230-V current will probably give better service than those that operate on 115 V, especially if the lower voltage circuit is only marginally adequate. Water baths and laboratory ovens with maximum operating temperatures of about 200°C perform well at 115 V. Care must be taken to ground all equipment that could constitute a shock hazard. The three-pronged plugs that incorporate grounds are best for this purpose.

2.7 References

1. Applebaum, S. B., and Crits, G. J., "Producing High Purity Water," Industrial Water Engineering (Sept./Oct. 1964).
2. "Water," Part 31 of 1977 Book of ASTM Standards, p. 20, American Society for Testing and Materials, Philadelphia (1977).

Chapter 3

INSTRUMENT SELECTION

3.1 Introduction

The modern analytical laboratory depends very heavily upon instrumentation. This statement may be completely obvious, but it should be remembered that the exceptional emphasis on electronic equipment has really begun since the development of the transistor and the computer. To a certain extent, analytical instrumentation is always in the development stage, with manufacturers continually redesigning and upgrading their products, striving for miniaturization, better durability and sensitivity, and improved automation. For laboratory supervisors and staff members the net result is a bewildering stream of advertising brochures, announcements, and catalogs of newly available equipment. Consequently, the selection of analytical equipment is always difficult.

The instruments commonly used in water and wastewater analysis include the following:

Analytical balance
pH/selective-ion meter
Conductivity meter
Turbidimeter
Spectrometers (visible, ultraviolet (UV), infrared (IR), and atomic absorption (AA))
Total carbon analyzer
Gas chromatograph (GC)
Gas chromatograph/mass spectrometer (GC/MS)
Temperature devices (such as ovens and water baths)
Recorders

These devices represent basic equipment used in routine work and should be the subject of careful consideration before purchase. Further, their operation and maintenance ought to be primary considerations in sustained production of satisfactory data. Obviously, fundamental understanding of instrument design will assist the analyst in the correct use of instruments and in some cases will aid in detecting instrumental failures. Calibration of all laboratory instruments with primary standards is encouraged whenever practical. This normally involves a National Bureau of Standards standard reference material or calibration and certification procedures. Calibration checks with secondary standards, made in each laboratory or available from private sources, are encouraged on a frequent basis if not required by the analytical method each time an analysis is made.

In the pages that follow an attempt is made to discuss basic instrument design and to offer some remarks about desirable instrumental features.

3.2 Analytical Balances

The most important piece of equipment in any analytical laboratory is the analytical balance. The degree of accuracy of the balance is reflected in the accuracy of all data related to weight-prepared standards. Although the balance should therefore be the most protected and cared-for instrument in the laboratory, proper care of the balance is frequently overlooked.

There are many fine balances on the market designed to meet a variety of needs. Types of balances include top-loading, two-pan, microanalytical, electroanalytical, semianalytical, analytical, and other special-purpose instruments. Each type of balance has its own place in the scheme of laboratory operation, but analytical single-pan balances are by far the most important in the production of reliable data.

Single-pan analytical balances range in capacity from the 20-g to the popular 200-g models with sensitivities from 0.01 to 1 mg. Features of single-pan balances may include mechanical and electronic switching of weights, digital readout, automatic zeroing of the empty balance, and automatic preweighing and taring capabilities. Even with all the design improvements, however, modern analytical balances are still fragile instruments, the operation of which is subject to shock, temperature, and humidity changes, to mishandling, and to various other insults. Some of the precautions to be observed in maintaining and prolonging the dependable life of a balance are as follows:

a. Analytical balances should be mounted on a heavy, shockproof table, preferably one with an adequately large working surface and with a suitable drawer for storage of balance accessories. The balance level should be checked frequently and adjusted when necessary.

b. Balances should be located away from laboratory traffic and protected from sudden drafts and humidity changes.

c. Balance temperatures should be equilibrated with room temperature; this is especially important if building heat is shut off or reduced during nonworking hours.

d. When the balance is not in use, the beam should be raised from the knife edges, the weights returned to the beam, objects such as the weighing dish removed from the pan, and the weighing compartment closed.

e. Special precautions should be taken to avoid spillage of corrosive chemicals on the pan or inside the balance case; the interior of the balance housing should be kept scrupulously clean.

f. Balances should be checked and adjusted periodically by a company service man or balance consultant; if service is not available locally, the manufacturer's instructions should be followed as closely as possible. Service contracts, including an automatic preventive maintenance schedule, are encouraged.

g. The balance should be operated at all times according to the manufacturer's instructions.

Standardized weights to be used in checking balance accuracy, traceable to the National Bureau of Standards, may be purchased from various supply houses. A complete set of directions for checking the performance of a balance is contained in part 41 of ASTM Standards (1).

Because all analytical balances of the 200-g capacity suitable for water and wastewater laboratories have about the same design specifications with reference to sensitivity, precision, convenience, and price, it is safe to assume that there is no clear preference for a certain model, and selection can be made on the basis of availability of service.

3.3 pH/Selective-Ion Meters

The concept of pH as a means of expressing the degree of *effective* acidity or alkalinity instead of *total* acidity or alkalinity was developed in 1909 by Sorenson (2). It was not until about 1940 that commercial instruments were developed for routine laboratory measurement of pH.

A basic meter consists of a voltage source, amplifier, and scale or digital readout device. Certain additional refinements produce varying performance characteristics between models. Some models incorporate expanded scales for increased readability, solid state circuitry for operating stability and extreme accuracy, and temperature and slope adjustment to correct for asymmetric potential of glass electrodes. Other features are scales that facilitate use of selective-ion electrodes, recorder output, and interfacing with complex data-handling systems.

In routine pH measurements the glass electrode is used as the indicator and the calomel electrode as the reference. Glass electrodes have a very fast response time in highly buffered solutions. However, accurate readings are obtained slowly in poorly buffered samples, and particularly so when changing from buffered to unbuffered samples. Electrodes, both glass and calomel, should be well rinsed with distilled water after each reading, and should be rinsed with, or dipped several times into, the next test sample before the final reading is taken. Weakly buffered samples should be stirred during measurement. When not in use, glass electrodes should not be allowed to become dry, but should be immersed in an appropriate solution consistent with the manufacturer's instructions. The first steps in calibrating an instrument are to immerse the glass and calomel electrodes into a buffer of known pH, set the meter to the pH of the buffer, and adjust the proper controls to bring the circuit into balance. The temperature-compensating dial should be set at the temperature of the buffer solution. For best accuracy, the instrument should be calibrated against two buffers that bracket the expected pH of the samples.

The presence of a faulty electrode is indicated by failure to obtain a reasonably correct value for the pH of the second reference buffer solution after the meter has been standardized with the first reference buffer solution. A cracked glass electrode will often yield pH readings that are essentially the same for both standards. The response of electrodes may also be impaired by failure to maintain the KCl level in the calomel electrode, by improper electrode maintenance, or by certain materials such as oily substances and precipitates that may coat the electrode surface. Faulty electrodes can often be restored to normal by an appropriate cleaning procedure. Complete and detailed cleaning methods are given in part 31 of ASTM Standards (3), and are also usually supplied by the electrode manufacturer.

Because of the asymmetric potential of the glass electrode, most pH meters are built with a slope adjustment that enables the analyst to correct for slight electrode errors observed during calibration with two different pH buffers. Exact details of slope adjustment and slope check may vary with different models of instruments. The slope adjustment must be made whenever electrodes are changed, subjected to vigorous cleaning, or refilled with fresh electrolyte. The slope adjustment feature is highly desirable and recommended for consideration when purchasing a new meter.

Most pH meters now available are built with transistorized circuits rather than vacuum tubes, which greatly reduces the warmup time and increases the stability of the meters.

Also, many instruments are designed with a switching circuit so that the entire conventional 0 to 14 scale of pH may be used to read a single pH unit with a corresponding increase in accuracy.

This expanded-scale feature is of definite value when the meter is used for potentiometric titrations and selective-ion work. It is of dubious value, however, in routine analyses, because pH readings more precise than ±0.1 are seldom required. 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 (3,4) such as the use of low-conductivity dilution water, drying ovens, and carbon-dioxide-free purge gas. These solutions should be replaced at least once each month.

Secondary standard buffers may be prepared from NBS salts or purchased as solutions from commercial vendors. Routine use of these commercially available solutions, which have been validated by comparison to NBS standards, is recommended.

The electrometric measurement of pH varies with temperature because of two effects. The first effect is the change in electrode output with temperature. This interference can be controlled by use of instruments having temperature compensation or by calibrating the instrument system including the electrode at the temperature of the samples. The second effect is the change of pH of the sample with temperature. 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.

Typical characteristics of a conventional expanded-scale meter are shown in table 3-1.

3.3.1 pH Electrodes

A wide variety of special- and general-purpose pH electrodes are now available to meet all applications in the general analytical laboratory. A survey through any laboratory supply catalog may confuse more than clarify the selection process. A rugged, full-range, glass- or plastic-bodied combination electrode is a good choice for routine use. An added convenience is an electrode that contains solid geltype filling materials not requiring the normal maintenance of an electrode containing liquid filling solutions.

3.3.2 Selective-Ion Electrodes

Electrodes have been developed to measure almost every common inorganic ion normally measured in the water and wastewater laboratory. Application of these electrodes has progressed at a much slower pace and currently only three are approved for EPA monitoring applications.

Reference 5 includes methods for use of fluoride, ammonia, and dissolved oxygen electrodes. Various techniques for use of these and other electrodes are reviewed in references 6 through 9. A major problem in measuring the total parameter with electrodes is that of relating the ion activity to ion concentration. Because the electrodes only measure

*NBS, Office of Standard Reference Materials, Institute for Materials Research, Washington, D.C. 20234.

Table 3-1
PERFORMANCE CHARACTERISTICS OF TYPICAL pH/SELECTIVE-ION METERS

Scale	Range		Smallest Scale Division		Accuracy		Reproducibility		Temperature Compensation[1] (°C)	Input Impedance (Ω)	Power Requirements	
	(pH)	(mV)	(pH)	(mV)	(pH)	(mV)	(pH)	(mV)			(V)	(Hz)
Normal	0-14	±1,400	0.1	10	±0.05	±5	±0.02	±2	0-100	>10	[2]115/220	50/60
Expanded	0-1	±100	.005	.5	±0.002	([3])	±0.002	±0.2	0-100	>10	[2]115/220	50/60

[1] Manual or automatic.
[2] May also be powered by self-contained batteries.
[3] ±2 percent of reading.

activity, the challenge is to put all of the parameters of interest into the same measurable ionic form and then to modify the activity to be proportional to the concentration. The technique of known addition (spiking of samples) is recommended when unproven electrode methods are being used or when sample matrix problems are suspected or not controlled by prior distillation or separation techniques.

3.4 Conductivity Meters

Solutions of electrolytes conduct an electric current by the migration of ions under the influence of an electric field. For a constant applied EMF, the current flowing between opposing electrodes immersed in the electrolyte will vary inversely with the resistance of the solution. The reciprocal of the resistance is called conductance and is expressed in reciprocal ohms (mhos). For natural water samples where the resistance is high, the usual reporting unit is micromhos.

Most conductivity meters on the market today use a cathode-ray tube, commonly known as the "magic eye," for indicating solution conductivity. A stepping switch for varying resistances in steps of 10X facilitates reading conductivities from about 0.1 to about 250,000 μmho. The sensing element for a conductivity measurement is the conductivity cell, which normally consists of two thin plates of platinized metal, rigidly supported with a very precise parallel spacing. For protection, the plates are mounted inside a glass tube with openings in the side walls and submersible end for access of sample. Variations in designs have included use of hard rubber and plastics for protection of the cell plates. Glass may be preferable, in that the plates may be visually observed for cleanliness and possible damage, but the more durable encasements have the advantage of greater protection and reduced cell breakage. Selection of various cell designs is normally based on personal preference with consideration of sample type and durability requirements.

In routine use, cells should be frequently examined to insure that (a) the platinized coating of plates is intact; (b) plates are not coated with suspended matter; (c) plates are not bent, distorted, or misalined; and (d) lead wires are properly spaced.

Temperature has a pronounced effect on the conductance of solutions, and must be corrected for when results are reported. The specified temperature for reporting data used by most analytical groups (and all EPA laboratories) is 25°C. Data correction may be accomplished by adjusting sample temperatures to 25°C, or by use of mathematical or electronic adjustment.

Instrumental troubles are seldom encountered with conductivity meters because of the design simplicity. When troubles occur, they are usually in the cell, and for most accurate work the following procedures should be used:

a. Standardize the cell and establish a cell factor by measuring the conductivity of a standard potassium chloride solution (standard conductivity tables may be found in various handbooks).

b. Rinse the cell by repeated immersion in distilled water.

c. Again, immerse the cell in the sample several times before obtaining a reading.

d. If the meter is equipped with a magic eye, determine the maximum width of the shadow at least twice, once by approaching the endpoint from a low reading upward, and once from a high reading downward.

Because the cell constants are subject to slow change even under ideal conditions, and sometimes to more rapid change under adverse conditions, it is recommended that the cell constant be periodically established. Table 3-2 can be used for this operation.

For instruments reading in mhos, the cell constant is calculated as follows:

$$L = \frac{K_1 + K_2}{10^6 K_x}$$

where

L = cell constant

K_1 = conductivity, in micromhos per centimeter, of the KCl solution at the temperature of measurement

K_2 = conductivity, in micromhos per centimeter, of the KCl solution at the same temperature as the distilled water used to prepare the reference solution

K_x = measured conductance, in mhos

Many different manufacturers produce conductivity meters that perform well on water and wastewater samples. Selection should be made consistent with sampling requirements, availability of service and sales, and individual personal preference.

3.5 Turbidimeters (Nephelometers)

Many different instrument designs have been used for the optical measurement of turbidity by measurement of either transmission or reflection of light. An equal or even greater

Table 3-2
ELECTRICAL CONDUCTIVITY OF POTASSIUM CHLORIDE REFERENCE SOLUTIONS

Solution	Normality	Method of Preparation	Temperature (°C)	Conductivity (μmho/cm)
A	0.1	7.4365 g/l KCl at 20°C	0	7,138
			18	11,167
			25	12,856
B	0.01	0.7440 g/l KCl at 20°C	0	773
			18	1,220
			25	1,408
C	0.001	Dilute 100 ml of B to 1.0 l at 20°C	25	147

number of materials have been used or proposed as calibration standards. As described in reference 10, EPA has standardized on the instrument design and the standard turbidity suspension of Formazin for instrument calibration.

Both the analyst and the user of turbidity data should keep in mind that a turbidity measurement is not a substitute for particle weight or residue analysis. Turbidity instruments can be calibrated to give gravimetric data on specific sample types, but the influence of particle geometry, specific gravity, refractive index, and color make estimates of total weight impractical on a variety of sample types.

For production of data with maximum accuracy and precision, the following precautions should be observed:

a. Protect the sample cuvette from scratches and fingerprints.

b. Use a constant orientation of the sample cuvette while calibrating the instrument and analyzing samples.

c. Use a well-mixed sample in the sample cuvette; do not take readings until finely dispersed bubbles have disappeared.

d. Dilute samples containing excess turbidity to some value below 40 nephelometric turbidity units (NTU); take reading; and multiply results by correct dilution factor.

3.6 Spectrometers

Because a large portion of routine quantitative measurements are performed colorimetrically, the spectrometer or filter photometer is usually the workhorse of any analytical laboratory. Indeed, the versatility of such instruments and the number of demands imposed upon them have resulted in a variety of designs and price ranges. Systematic listing and detailed discussion of all instrumental types are beyond the scope of this chapter; however, ultraviolet, visible, infrared, and atomic absorption instruments will be discussed.

A spectrometer is an instrument for measuring the amount of light or radiant energy transmitted through a solution or solid material as a function of wavelength. A spectrometer differs from a filter photometer in that it uses continuously variable, and more nearly monochromatic, bands of light. Because filter photometers lack the versatility of spectrometers, they are used most profitably where standard methodologies are used for routine analysis.

The essential parts of a spectrometer include the following:

a. A source of radiant energy

b. Monochromator or other device for isolating narrow spectral bands of light

c. Cells (cuvettes) or sample holders for containing samples under investigation

d. A photodetector (a device to detect and measure the radiant energy passing through the sample)

Each of the essential features listed, especially the monochromator and the photodetector system, varies in design principles from one instrument to another. Some of the characteristics of the commonly used Perkin-Elmer model 124 double-beam grating spectrometer are the following:

Light source	
Visible region	Tungsten
Lamp UV region	Deuterium lamp
Wavelength accuracy	±0.5 nm
Spectral bandwidth	0.5, 1.0, and 2.0 nm
Photometric presentation	
Linear transmittance	0 to 100 percent
Linear absorbance	0 to 1*A* or 0 to 2*A*
Photodetector R-136	190 to 800 nm
Sample cells	1.0 to 10 cm

3.6.1 Visible Range

Desirable features on a visible-range spectrometer are determined by the anticipated use of the instrument. Simple, limited programs requiring use of only a few parameters can probably be supported by inexpensive but reliable filter photometers. On the other hand, if the laboratory programs require a wide variety of measurements on diverse samples at low concentrations, more versatile instruments may be needed. One of the prime considerations is adaptability to various sample cell sizes from 1.0 to 10.0 cm.

3.6.2 Ultraviolet Range

A UV spectrometer is similar in design to a visible-range instrument except for differences in the light source and in the optics. The UV light source is a hydrogen- or deuterium-discharge lamp, which emits radiation in the UV portion of the spectrum, generally from about 200 nm to the low-visible-wavelength region. The optical system and sample cells must be constructed of UV-transparent material, which is usually quartz. A grating used in a UV system may be specially cut (blazed) in the UV region for greater sensitivity.

3.6.3 Infrared Range

A number of instrumental modifications are required in the construction of spectrometers for measurements in the IR region because materials such as glass and quartz absorb IR radiant energy, and ordinary photocells do not respond to it. Most IR spectrometers use front-surfaced mirrors to eliminate the necessity for the transmission of radiant energy through quartz, glass, or other lens materials. These mirrors are usually parabolic to focus the diffuse IR energy. Such instruments must be protected from high humidities and water vapor to avoid deterioration of the optical system and the presence of extraneous absorption bands in the IR.

The energy or light source for an IR instrument may be a Nernst glower or a Globar. Each of these sources has certain characteristics that recommend it for use, but the more rugged Globar is more commonly used because it also has a more stable emission. The receiving or detection unit may be a thermocouple, bolometer, thermistor, or photoconductor cell. The type of analysis being performed dictates the degree of sophistication required in the IR instrumentation selected to acquire usable data.

3.6.4 Proper Use of Spectrometers

The spectrometer manufacturer's instructions for proper use should be followed in all cases. Several safeguards against misuse of the instruments, however, are mandatory.

Instruments should be checked for wavelength alinement. If a particular colored solution is to be used at a closely specified wavelength, considerable loss of sensitivity can be encountered if the wavelength control is misalined. In visible-range instruments, an excellent reference point is the maximum absorption for a diluted solution of potassium permanganate, which has dual peaks at 526 and 546 nm. On inexpensive instruments with less resolution the permanganate peak appears at 525 to 550 nm as a single, flat-topped peak.

For both UV and IR instruments, standard absorption curves for many organic materials have been published so that reference material for standard peaks is easily available. Standard films of styrene and other transparent plastics are available for IR wavelength checks. A very good discussion of factors that affect the proper performance of spectrometers and standard reference materials available to calibrate them can be found in publications of the National Bureau of Standards.* Use of certified standards is encouraged whenever practical.

Too much emphasis cannot be placed on care of absorption cells. All absorption cells should be kept scrupulously clean, free of scratches, fingerprints, smudges, and evaporated film residues. Matched cells should be checked to see that they are equivalent, and any differences should be accounted for during use or in the final data. Directions for cleaning cells are given in chapter 4.

Generally speaking, trained technicians may operate any of the spectrometers successfully; however, because interpretation of data from both the UV and IR instruments is becoming increasingly complex, mere compliance with the operations manual may not be sufficient for completely accomplishing the special techniques of sample preparation, instrument operation, and interpretation of absorption curves.

3.6.5 Atomic Absorption

There are a number of differences in the basic design and accessories for atomic absorption (AA) equipment that require consideration before purchase and during subsequent use. These choices concern the light sources, nebulizer burners, optical systems, readout devices, and mode conversions. Because some of these choices are not readily obvious, the purchaser or user must be familiar with the types and numbers of samples to be analyzed and the

*NBS, Office of Standard Reference Materials, Institute for Materials Research, Washington, D.C. 20234.

specific elements to be measured before making the choice. For a program analyzing a wide variety of samples for a number of elements at varying concentrations, an instrument of maximum versatility would be best. Most of the discussion that follows applies to use of instrumentation in absorption, emission, or fluorescence modes.

3.6.5.1 Lamps

Hollow-cathode (HC) lamps or electrodeless-discharge lamps (EDL) are available for over 70 elements with single-element or multielement capability. Multielement lamps are considerably cheaper per element than single-element lamps, but the savings may not be realized if the lamps are not used strategically, because all the elements in the cathode deteriorate when the lamp is used, regardless of which element is measured. The deterioration phenomena result from the different volatilities of metals used in the cathode. One metal volatilizes (sputters) more rapidly than the others and redeposits upon an area of the other cathode metals. Thus, with continual use, a drift in signal will be noted with at least one metal increasing and the other (or others) decreasing. If one can ignore the dubious cost savings of multielement lamps, use of single-element lamps could result in more precise and accurate data.

The line intensities of one element in a multielement HC lamp will usually be less than those of a lamp containing a pure cathode of the same element because this element must share the discharge energy with the other elements present. However, this reduction should not affect the output by a factor of more than one-sixth to one-half, depending on the particular combination and the number of elements combined. The output can be even greater in some multielement lamps because alloying may permit a higher operating current than for the case of the pure cathode. All HC lamps have life expectancies that are related to the volatility of the cathode metal, and for this reason the manufacturer's recommendations for operating should be closely followed.

Recent improvements in design and manufacture of HC lamps and EDLs have resulted in lamps with more constant output and longer life. Under normal conditions an HC lamp may be expected to operate satisfactorily for several years. HC lamps used to be guaranteed for a certain minimum ampere-hour period, but this has been changed to a 90-day warranty. It is good practice to date newly purchased lamps and to inspect them immediately upon receipt. The operating current and voltage indicated on the lamp should not be exceeded during use. An increase in background noise or a loss of sensitivity are signs of lamp deterioration.

A basic design feature of AA spectrometers is the convenience of the HC lamp changeover system. Some instruments provide for as many as six lamps in a rotating turret, all electronically stabilized and ready for use by simply rotating the lamp turret. Other instruments provide for use of only one lamp at a time in the lamp housing, and require manual removal and replacement whenever more than one element is to be measured. A quick-changeover system enables frequent lamp changes during the period of operation. If necessary lamp changes are infrequent, however, multilamp mounts do not represent a great convenience.

After the proper lamp has been selected, the HC current should be adjusted according to the manufacturer's recommendations and allowed to electronically stabilize (warm up) before use. During this 15-min period, the monochromator may be positioned at the correct wavelength, and the proper slit width may be selected. For those instruments employing a multilamp turret, a warmup current is provided to those lamps not in use, thereby

minimizing the warmup period after the turret is rotated. In a single-lamp instrument, the instability exhibited during warmup is minimized by the use of a double-beam optical system.

3.6.5.2 Burner Types

The most difficult and inefficient step in the AA process is converting the metal in the sample from an ion or a molecule to the neutral atomic state. It is the function of the atomizer/burner to produce the desired neutral atomic condition of the elements. With minor modifications burners are the same as those used for flame photometry.

Basically there are two different types of burners. They are the total-consumption, or surface-mix burner, and the laminar-flow or premix burner. There are many variations of these two basic types, such as the Boling, the high-solids, the turbulent-flow, the triflame, the nitrous oxide burners, and many others. As one might expect, there are many similarities among the various burners, the different names resulting from the different manufacturers. The element being determined and the type of sample solution dictate the type of burner to be used. Generally, all types and makes of burner can be adjusted laterally, rotationally, and vertically for selection of the most sensitive area of the flame for the specific element sought.

Nonflame techniques have gained wide acceptance in AA analysis because of the extreme sensitivity and the capability to directly introduce very diverse sample matrices. These systems, which replace the conventional flame burner, come in various designs using electrical resistance to produce temperatures as high as 3,500°C.

3.6.5.3 Single- and Double- (Split-) Beam Instruments

There is a great deal of existing uncertainty among instrument users about the relative merits of single- and double-beam instruments. Neither system is appropriate for all cases.

With a single-beam instrument the light beam from the source passes directly through the flame to the detector. In a double-beam system the light from the source is divided by a beam splitter into two paths. One path, the reference beam, goes directly to the detector. The second path, the sample beam, goes through the flame to the detector. The chopper alternately reflects and passes each beam, creating two equal beams falling alternately upon the detector. If the beams are equal, they cancel the alternate impulses reaching the detector, and no signal is generated. If the beams are different, the resulting imbalance causes the detector to generate a signal that is amplified and measured. The difference between the reference and sample beams is then determined as a direct function of absorbed light. The advantages of the double-beam design are that any variations in the source are of reduced importance, and smaller dependence is placed upon the stability of the power supply. Conversely, stabilization of the power supply can eliminate the apparent need for the split-beam system. Furthermore, the beam splitter requires additional mirrors or optical accessories that cause some loss of radiant energy.

A single-beam system does not monitor source variations, but offers certain other advantages. It allows use of low-intensity lamps, smaller slit settings, and smaller gain. As a consequence, the single-beam instrument, properly designed, is capable of operating with lower noise and better signal-to-noise ratio, and therefore with better precision and improved sensitivity. Because the simplified optical system conserves radiant energy,

especially in the shorter wavelengths, it facilitates operation in the low-wavelength range. With this advantage, it should be possible to obtain better sensitivity for those elements with a strong resonance line below 350 nm and particularly those below 300 nm. Background correction techniques are also available in single-beam systems.

Double-beam instruments, however, offer the opportunity to perform more sophisticated techniques like background correction, two-channel multielement analysis, use of internal standards, and element rationing. If one of these techniques is necessary, a double-beam instrument must be considered.

3.6.5.4 Readout Devices

Readout devices in even the lower cost AA instruments include digital concentration display. Using high-speed digital electronics, data-handling techniques encompass multiple calibration standards, regression analysis to characterize the calibration curves, mean variance and standard deviation statistical programs for sample calculations, and various forms of printout reports in addition to recorder output. Choice of a readout system is predicated largely upon laboratory needs and availability of budget. In general, any step toward automation is desirable, but the degree of automation should be compatible with the laboratory program.

3.6.5.5 Miscellaneous Accessories

A number of instruments contain a mode selector, making an instrument usable for either absorption or emission. The conversion to emission may be a desirable feature because certain elements are more amenable to analysis by this method. Some models offer an option of atomic fluorescence and can also be used as a UV/visible spectrometer.

Automatic sample changers are offered for almost all instruments on the market, and as has been previously stated, any automation feature is desirable. However, unless a laboratory program performs a large number of repetitious measurements daily, an automatic sample changer is not required. As a practical measure, other commonly used sample-changing devices, although not expressly designed for AA use, can be interfaced with most AA instruments.

3.7 Organic Carbon Analyzers

A number of instruments designed to measure total organic carbon (TOC) in waters and wastes have appeared on the market in the past several years. The first of these units involved pyrolysis followed by IR measurement of the carbon dioxide formed. Sample injection of 20 to 200 μl in a carrier gas of air or oxygen was performed with a syringe. Combustion at 800°C to 900°C followed by IR analysis was performed automatically with final output on an analog recorder. Systems using these principles are still produced and represent a large part of the TOC market.

Other techniques of TOC analysis that modify every phase of the original TOC instruments have been introduced. Sample presentation in small metallic boats and purging of CO_2 from solution are two new techniques. Wet chemical oxidation, either external to the instrument or within the instrument, using various oxidants including ultraviolet irradiation is now in wide use. Measurement of the CO_2 by reduction to methane (CH_4) and quantitation with a flame ionization detector are also available. Various methods of data handling are now used,

ranging from recorder output to direct readings and printouts of concentration. Techniques are also available for measuring materials like soil and sludges, and also the volatile component of the TOC. Sensitivity on some systems has been extended down to the microgram per liter level. The major problems associated with TOC measurements are interference from forms of inorganic carbon and the difficulty of obtaining a representative sample in the presence of particulate matter. Each system has its own procedure for sample pretreatment or for accounting for these problems. When choosing a TOC instrument, consideration should be given to the types of samples to be analyzed, the expected concentration range, and the forms of carbon to be measured.

3.8 Gas Chromatographs

Because GC's are available from a large number of manufacturers, selection of a particular manufacturer may be based on convenience. No single multipurpose GC instrument permits analysis of a wide range of compounds. In this case, a GC/MS could be considered (11). If, however, relatively few types of environmentally significant compounds are being surveyed, an inexpensive system equipped with a glass-lined injection port, electrolytic conductivity detector, and analog recorder is a good choice. A review of the organic methods (12) to be used will give the analyst all the necessary information on the specific instrument, apparatus, and materials necessary for each type or class of compounds. A discussion of various quality control considerations in GC analysis is given in chapter 8 of this manual.

Data handling requirements vary widely, and the need to automate GC data collection is determined by the extent of the sample load. In a routine monitoring laboratory, GC systems incorporating their own microprocessers and report generating capabilities would be useful in solving this problem. Because such systems greatly increase the cost, the overall economy of this choice must be considered.

3.9 References

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Chapter 4

GLASSWARE

4.1 General

The measurement of trace constituents in water demands methods capable of maximum sensitivity. This is especially true for metals and trace organics such as pesticides, as well as for the determination of ammonia and phosphorus. In addition to sensitive methods, however, there are other areas that require special consideration. One such area is that of the cleanliness of laboratory glassware. Obviously, the very sensitive analytical systems are more sensitive to errors resulting from the improper use or choice of apparatus, as well as to contamination effects due to an improper method of cleaning the apparatus. The purpose of this chapter is to discuss the kinds of glassware available, the use of volumetric ware, and various cleaning requirements.

4.2 Types of Glassware

Laboratory vessels serve three functions: storage of reagents, measurement of solution volumes, and confinement of reactions. For special purposes, vessels made from materials such as porcelain, nickel, iron, aluminum, platinum, stainless steel, and plastic may be employed to advantage. Glass, however, is the most widely used material of construction. There are many grades and types of glassware from which to choose, ranging from student grade to others possessing specific properties such as super strength, low boron content, and resistance to thermal shock or alkali. Soft glass containers are not recommended for general use, especially for storage of reagents because of the possibility of dissolving of the glass (or of some of the constituents of the glass). The mainstay of the modern analytical laboratory is a highly resistant borosilicate glass, such as that manufactured by Corning Glass Works under the name "Pyrex" or by Kimble Glass Co. as "Kimax." This glassware is satisfactory for all analyses included in reference 1.

Depending on the particular manufacturer, various trade names are used for specific brands possessing special properties such as resistance to heat, shock, and alkalies. Examples of some of these special brands follow:

a. Kimax- or Pyrex-brand glass is a relatively inert all-purpose borosilicate glass.

b. Vycor-brand glass is a silica glass (96 percent) made to withstand continuous temperatures up to 900°C and can be down-shocked in ice water without breakage.

c. Corning-brand glass is claimed to be 50 times more resistant to alkalies than conventional ware and practically boron-free (maximum 0.2 percent).

d. Ray-Sorb- or Low-Actinic-brand glass is used when the reagents or materials are light sensitive.

e. Corex-brand labware is harder than conventional borosilicates and therefore better able to resist clouding and scratching.

The use of plastic vessels, containers, and other apparatus made of Teflon, polyethylene, polystyrene, and polypropylene has increased markedly over recent years. Some of these

materials, such as Teflon, are quite expensive; however, Teflon stopcock plugs have practically replaced glass plugs in burets, separatory funnels, etc., because lubrication to avoid sticking or "freezing" is not required. Polypropylene, a methylpentene polymer, is available as laboratory bottles, graduates, beakers, and even volumetric flasks. It is crystal clear, shatterproof, autoclavable, and chemically resistant.

The following are some points to consider in choosing glassware or plasticware:

a. The special types of glass listed above, other than Pyrex or Kimax, generally are not required to perform the analyses given in "Methods for Chemical Analysis of Water and Wastes" (1).

b. Unless instructed otherwise, borosilicate or polyethylene bottles may be used for the storage of reagents and standard solutions.

c. Dilute metal solutions are prone to plate out on container walls over long periods of storage. Thus, dilute metal standard solutions must be prepared fresh at the time of analysis.

d. For some operations, disposable glassware is entirely satisfactory. One example is the use of disposable test tubes as sample containers for use with the Technicon automatic sampler.

e. Plastic bottles of polyethylene and Teflon have been found satisfactory for the shipment of water samples. Strong mineral acids (such as sulfuric acid) and organic solvents will readily attack polyethylene and are to be avoided.

f. Borosilicate glassware is not completely inert, particularly to alkalies; therefore, standard solutions of silica, boron, and the alkali metals are usually stored in polyethylene bottles.

For additional information the reader is referred to the catalogs of the various glass and plastic manufacturers. These catalogs contain a wealth of information such as specific properties, uses, and sizes.

4.3 Volumetric Analyses

By common usage, accurately calibrated glassware for precise measurements of volume has become known as volumetric glassware. This group includes volumetric flasks, volumetric pipets, and accurately calibrated burets. Less accurate types of glassware including graduated cylinders and serological and measuring pipets also have specific uses in the analytical laboratory when exact volumes are unnecessary.

The precision of volumetric work depends in part upon the accuracy with which volumes of solutions can be measured. There are certain sources of error that must be carefully considered. The volumetric apparatus must be read correctly; that is, the bottom of the meniscus should be tangent to the calibration mark. There are other sources of error, however, such as changes in temperature, which result in changes in the actual capacity of glass apparatus and in the volume of the solutions. The capacity of an ordinary glass flask of 1000-ml volume increases 0.025 ml/deg with rise in temperature, but if the flask is made of borosilicate glass, the increase is much less. One thousand milliliters of water or of most 0.1*N* solutions increases in volume by approximately 0.20 ml/deg increase at room

temperature. Thus solutions must be measured at the temperature at which the apparatus was calibrated. This temperature (usually 20°C) will be indicated on all volumetric ware. There may also be errors of calibration of the apparatus; that is, the volume marked on the apparatus may not be the true volume. Such errors can be eliminated only by recalibrating the apparatus or by replacing it.

Volumetric apparatus is calibrated to contain or to deliver a definite volume of liquid. This will be indicated on the apparatus with the letters "TC" (to contain) or "TD" (to deliver). Volumetric flasks are calibrated to contain a given volume and are available in various shapes and sizes.

Volumetric pipets are calibrated to deliver a fixed volume. The usual capacities are 1 through 100 ml although micropipets are also available. Micropipets are most useful in furnace work and are available in sizes ranging from 1 to 100 μl.

In emptying volumetric pipets, they should be held in a vertical position and the outflow should be unrestricted. The tip of the pipet is kept in contact with the wall of the receiving vessel for a second or two after the free flow has stopped. *The liquid remaining in the tip is not removed*; this is most important.

Measuring and serological pipets should also be held in a vertical position for dispensing liquids; however, the tip of the pipet is only touched to the wet surface of the receiving vessel after the outflow has ceased. For those pipets where the small amount of liquid remaining in the tip is to be blown out and added, indication is made by a frosted band near the top.

Burets are used to deliver definite volumes. The more common types are usually of 25- or 50-ml capacity, graduated to tenths of a milliliter, and are provided with stopcocks. For precise analytical methods in microchemistry, microburets are also used. Microburets generally are of 5- or 10-ml capacity, graduated in divisions of hundredths of a milliliter. Automatic burets with reservoirs are also available ranging in capacity from 10 to 100 ml. Reservoir capacity ranges from 100 to 4,000 ml.

General rules in regard to the manipulation of a buret are as follows: Do not attempt to dry a buret that has been cleaned for use, but rinse it two or three times with a small volume of the solution with which it is to be filled. Do not allow alkaline solutions to stand in a buret because the glass will be attacked, and the stopcock, unless made of Teflon, will tend to freeze. A 50-ml buret should not be emptied faster than 0.7 ml/s, otherwise too much liquid will adhere to the walls and as the solution drains down, the meniscus will gradually rise, giving a high false reading. It should be emphasized that improper use or reading of burets can result in serious calculation errors.

In the case of all apparatus for delivering liquids, the glass must be absolutely clean so that the film of liquid never breaks at any point. Careful attention must be paid to this fact or the required amount of solution will not be delivered. The various cleaning agents and their use are described later.

4.4 Federal Specifications for Volumetric Glassware

Reference 2 contains a description of Federal specifications for volumetric glassware. The National Bureau of Standards no longer accepts stock quantities of volumetric apparatus

from manufacturers or dealers for certification and return for future sale to consumers. This certification service is still available, but apparatus will be tested only when submitted by the ultimate user, and then only after an agreement has been reached with the Bureau concerning the work to be done.

Consequently, the various glass manufacturers have discontinued the listing of NBS-certified ware. In its place catalog listings of volumetric glass apparatus that meet the Federal specifications are designated as class A and all such glassware is permanently marked with a large "A." These NBS specifications are listed in table 4-1. The glassware in question includes the usual burets, volumetric flasks, and volumetric pipets.

In addition to the "A" marking found on calibrated glassware and the temperature at which the calibration was made, other markings also appear. These include the type of glass, such

Table 4-1
TOLERANCES FOR VOLUMETRIC GLASSWARE[1]

Type of Glassware	Capacity[2] (ml)	Limit of Error (ml)
Graduated flask	25	0.03
	50	0.05
	100	0.08
	200	0.10
	250	0.11
	300	0.12
	500	0.15
	1,000	0.30
	2,000	0.50
Transfer pipet	2	0.006
	5	0.01
	10	0.02
	25	0.025
	30	0.03
	50	0.05
	100	0.08
	200	0.10
Buret[3]	5	0.01
	10	0.02
	30	0.03
	50	0.05
	100	0.10

[1] Abridged from reference 3.
[2] Less than and including.
[3] Limits of error are of total or partial capacity. Customary practice is to test the capacity at five intervals.

as Pyrex, Corex, or Kimax; the stock number of the particular item; and the capacity of the vessel. If the vessel contains a ground-glass connection, this will also be included along with the TD or TC symbol. An example of the markings usually found on volumetric ware is shown in figure 4-1. Class A glassware need not be recalibrated before use. However, if it should become necessary to calibrate a particular piece of glassware, directions may be found in texts (4) on quantitative analysis.

4.5 Cleaning of Glass and Porcelain

The method of cleaning should be adapted to both the substances that are to be removed, and the determination to be performed. Water-soluble substances are simply washed out with hot or cold water, and the vessel is finally rinsed with successive small amounts of distilled water. Other substances more difficult to remove may require the use of a detergent, organic solvent, dichromate cleaning solution, nitric acid, or aqua regia (25 percent by volume concentrated HNO_3 in concentrated HCl). In all cases it is good practice to rinse a vessel with tap water as soon as possible after use. Material allowed to dry on glassware is much more difficult to remove.

Volumetric glassware, especially burets, may be thoroughly cleaned by a mixture containing the following: 30 g of sodium hydroxide, 4 g of sodium hexametaphosphate (trade name, Calgon), 8 g of trisodium phosphate, and 1 l of water. A gram or two of sodium lauryl sulfate or other surfactant will improve its action in some cases. This solution should be used with a buret brush.

Dichromate cleaning solution (chromic acid) is a powerful cleaning agent; however, because of its destructive nature upon clothing and upon laboratory furniture, extreme care must be taken when using this mixture. If any of the solution is spilled, it must be cleaned up immediately. Chromic acid solution may be prepared in the laboratory by adding 1 l of concentrated sulfuric acid slowly, with stirring, to a 35-ml saturated sodium dichromate solution. This mixture must be allowed to stand for approximately 15 min in the vessel that is being cleaned and may then be returned to a storage bottle. Following the chromic acid wash, the vessels are rinsed thoroughly with tap water, then with small successive portions of distilled water. The analyst should be cautioned that when chromium is included in the

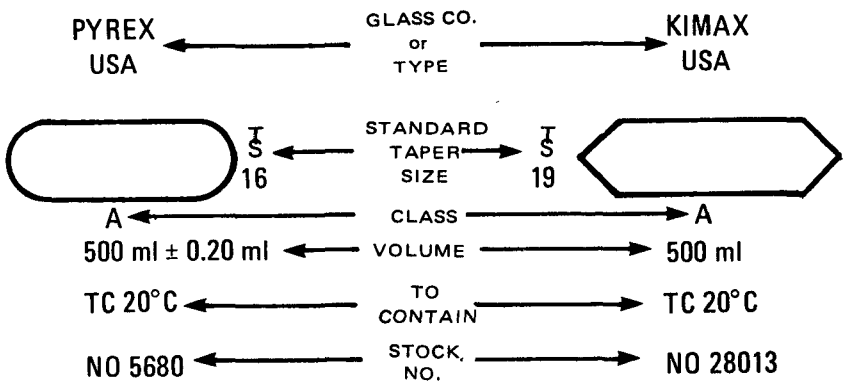

Figure 4-1. Example of markings on glassware.

scheme of analysis, it is imperative that the last traces of dichromate be removed from the apparatus. To this end, a substitute for dichromate cleaning solution, called Nochromix,* is available and may be used to advantage. Fuming nitric acid is another powerful cleaning agent, but is disagreeable to handle. As with dichromate, when the acid becomes dilute, the cleaning mixture is no longer effective. A mixture of concentrated sulfuric and fuming nitric acids is even more efficient but is also hazardous to use. A persistent greasy layer or spot may be removed by acetone or by allowing a warm solution of sodium hydroxide, about 1 g per 50 ml of water, to stand in the vessel for 10 to 15 min; after rinsing with water, dilute hydrochloric acid, and water again, the vessel is usually clean. Alcoholic potassium hydroxide is also effective in removing grease. To dry glass apparatus, rinse with acetone and blow or draw air through it.

4.6 Special Cleaning Requirements

Absorption cells, used in spectrophotometers, should be kept scrupulously clean, free of scratches, fingerprints, smudges, and evaporated film residues. The cells may be cleaned with detergent solutions for removal of organic residues, but should not be soaked for prolonged periods in caustic solutions because of the possibility of etching. Organic solvents may be used to rinse cells in which organic materials have been used. Nitric acid rinses are permissible, but dichromate solutions are not recommended because of the adsorptive properties of dichromate on glass. Rinsing and drying of cells with alcohol or acetone before storage is a preferred practice. Matched cells should be checked to see that they are equivalent by placing portions of the same solution in both cells and taking several readings of the transmittance (T, percent) or optical density (OD) values.

For certain determinations, especially trace metals, the glassware should also be rinsed with a 1:1 nitric acid-water mixture. This operation is followed by thoroughly rinsing with tap water and successive portions of distilled water. This may require as many as 12 to 15 rinses, especially if chromium is being determined. The nitric acid rinse is also especially important if lead is being determined.

Glassware to be used for phosphate determinations should not be washed with detergents containing phosphates. This glassware must be thoroughly rinsed with tap water and distilled water. For ammonia and Kjeldahl nitrogen, the glassware must be rinsed with ammonia-free water. (See ch. 2.)

Glassware to be used in the determination of trace organic constituents in water, such as chlorinated pesticides, should be as free as possible of organic contaminants. A chromic acid wash of at least 15 min is necessary to destroy these organic residues. Rinse thoroughly with tap water and, finally, with distilled water. Glassware may be dried for immediate use by rinsing with redistilled acetone. Otherwise glassware may be oven dried or drip dried. Glassware should be stored immediately after drying to prevent any accumulation of dust and stored inverted or with mouth of glassware covered with foil.

Bottles to be used for the collection of samples for organic analyses should be rinsed successively with chromic acid cleaning solution, tap water, distilled water, and, finally, several times with a redistilled solvent such as acetone, hexane, petroleum ether, or chloroform. Caps are washed with detergent, rinsed with tap water, distilled water, and

*Available from Godax Laboratories, 6 Varick Street, New York, N.Y. 10013.

solvent. Liners are treated in the same way as the bottles and are stored in a sealed container.

4.7 Disposable Glassware

When the risk of washing a pipet for reuse becomes too great, as in the case of use with toxic materials, or when the cost of washing glassware becomes prohibitive, disposable vessels may be the answer, provided they meet the necessary specification. Various types are available including bacteriological, serological, and microdilution pipets. Disposable glassware generally is made of soft glass although plastic vessels and pipets are also available.

4.8 Specialized Glassware

The use of vessels and glassware fitted with standard-taper, ground-glass, and ball-and-socket joints has increased because of certain advantages such as less leakage and fewer freezeups. Standard-taper, interchangeable ground joints save time and trouble in assembling apparatus. They are precision-ground with tested abrasives to insure an accurate fit and freedom from leakage. Ball and socket joints increase flexibility of operation and eliminate the need for exact alinements of apparatus. Symbols and their meaning as applied to standard joints, stoppers, and stopcocks are shown below.

4.8.1 Standard Taper (⧖)

The symbol ⧖ is used to designate interchangeable joints, stoppers, and stopcocks that comply with the requirements of reference 5. All mating parts are finished to a 1:10 taper.

The size of a particular piece appears after the appropriate symbol. Primarily because of greater variety of apparatus equipped with ⧖ fittings, a number of different types of identifications are used:

a. For joints—a two-part number as ⧖ 24/40, with 24 being the approximate diameter in millimeters at the large end of the taper and 40 the axial length of taper, also in millimeters

b. For stopcocks—a single number, as ⧖ 2, with 2 mm being the approximate diameter of the hole or holes through the plug

c. For bottles—a single number, as ⧖ 19, with 19 mm being the appropriate diameter at top of neck. However, there are differences in dimensions between the bottle and flask stoppers

d. For flasks and similar containers—a single number, as ⧖ 19, with 19 mm being the appropriate diameter of the opening at top of neck

4.8.2 Spherical Joints (§)

The designation § is for spherical (semiball) joints complying with reference 5. The complete designation of a spherical joint also consists of a two-part number, as 12/2, with 12 being the approximate diameter of the ball and 2 the bore of the ball and the socket, also in millimeters.

4.8.3 Product Standard (§)

The symbol § is used for stopcocks with Teflon plugs, the mating surfaces being finished to a 1:5 taper. As with ℨ stopcocks, a single number is used. Thus, § 2 means a Teflon stopcock with a hole of approximately 2-mm diameter in the plug.

4.9 Fritted Ware

For certain laboratory operations the use of fritted ware for filtration, gas dispersion, absorption, or extractions may be advantageous.

There are six different porosities of fritted ware available, depending on its intended use. Porosity is controlled in manufacture, and disks are individually tested and graded into these classifications. The extra-coarse and coarse porosities are held toward the maximum pore diameter as listed. The medium, fine, very fine, and ultrafine are held toward the minimum pore diameter as listed in table 4-2.

Pore sizes are determined by the method specified in reference 6.

4.9.1 Recommended Procedures for Maximum Filter Life

a. New Filters. Wash new filters by suction with hot hydrochloric acid, followed by a water rinse.

b. Pressure Limits. The maximum, safe, differential pressure on a disk is 15 lb/in^2.

c. Thermal Shock. Fritted ware has less resistance to thermal shock than nonporous glassware. Hence, excessive, rapid temperature changes and direct exposure to a flame should be avoided. Heating in a furnace to 500°C may be done safely, provided the heating and cooling are gradual. Dry ware may be brought to constant weight by heating at 105°C to 110°C.

Never subject a damp filter of ultrafine porosity to a sudden temperature change. Steam produced in the interior may cause cracking.

Table 4-2
FRITTED-WARE POROSITY

Porosity Grade	Designation	Pore Size (μm)	Principal Uses
Extra Coarse	EC	170-220	Coarse filtration; gas dispersion, washing, and absorption
Coarse	C	40-60	Coarse filtration; gas dispersion, washing, and absorption
Medium	M	10-15	Filtration and extraction
Fine	F	4-5.5	Filtration and extraction
Very Fine	VF	2-2.5	General bacterial filtration
Ultrafine	UF	0.9-1.4	General bacterial filtration

4.9.2 Cleaning of Used Filters

In many cases, precipitates can be removed by rinsing with water, passed through from the underside, with the pressure not exceeding 15 lb/in^2. The suggestions that follow will be helpful in dealing with material that will not be removed by such a reverse water-wash:

Material	*Removal Agent*
Albumen	Hot ammonia or hydrochloric acid
Aluminous and siliceous residues	Hydrofluoric acid (2 percent) followed by concentrated sulfuric acid; rinse immediately with water until no trace of acid can be detected.
Copper or iron oxides	Hot hydrochloric acid plus potassium chlorate
Fatty materials	Carbon tetrachloride
Mercuric sulfide	Hot aqua regia
Organic matter	Hot, concentrated cleaning solution, or hot, concentrated sulfuric acid with a few drops of sodium nitrite
Silver chloride	Ammonium or sodium hyposulfite

4.10 References

1. Methods for Chemical Analysis of Water and Wastes, U.S. EPA, Office of Research and Development, EMSL (1978).
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Chapter 5

REAGENTS, SOLVENTS, AND GASES

5.1 Introduction

The objective of this chapter is to provide general information and suggestions that will serve to keep the analyst conscious of his responsibilities in analytical quality control, as they relate to reagents, solvents, and gases. While the material presented here will assist the analyst in producing high-quality data, it is by no means complete. It is incumbent on the analyst to obtain details of special precautions required to insure proper selection, preparation, and storage of reagents, solvents, and gases from the descriptions of individual methods.

5.2 Reagent Quality

Chemical reagents, solvents, and gases are available in a wide variety of grades of purity, ranging from technical grade to various ultrapure grades. The purity of these materials required in analytical chemistry varies with the type of analysis. The parameter being measured and the sensitivity and specificity of the detection system are important factors in determining the purity of the reagents required. For many analyses, including most inorganic analyses, analytical reagent grade is satisfactory. Other analyses, such as trace organic and radiological, frequently require special ultrapure reagents, solvents, and gases. In methods where the purity of reagents is not specified it is intended that analytical reagent grade be used. Reagents of lesser purity than that specified by the method should not be used. The labels on the container should be checked and the contents examined to verify that the purity of the reagents meets the needs of the particular method involved. The quality of reagents, solvents, and gases required for the various classes of analyses—inorganic, metals, radiological, and organic—are discussed in this section.

Reagents must always be prepared and standardized with the utmost of care and technique against reliable primary standards. They must be restandardized or prepared fresh as often as required by their stability. Stock and working standard solutions must be checked regularly for signs of deterioration; e.g., discoloration, formation of precipitates, and change of concentration. Standard solutions should be properly labeled as to compound, concentration, solvent, date, and preparer.

Primary standards must be obtained from a reliable source, pretreated (e.g., dried, under specified conditions), accurately prepared in calibrated volumetric glassware, and stored in containers that will not alter the reagent. A large number of primary standards are available from the National Bureau of Standards (NBS). A complete listing of available standards is given in reference 1. Primary standards may also be obtained from many chemical supply companies. Suppliers for special quality reagents, solvents, and gases are noted in later discussions of the various classes of analyses. Reagents and solvents of all grades are available from many chemical supply houses.

There is some confusion among chemists as to the definition of the terms "Analytical Reagent Grade," "Reagent Grade," and "ACS Analytical Reagent Grade." A review of the literature and chemical supply catalogs indicates that the three terms are synonymous. Hereafter, in this document, the term "Analytical Reagent Grade" (AR) will be used. It is

intended that AR-grade chemicals and solvents shall conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society (2).

References 3 through 5 devote several chapters to problems related to preparation, standardization, and storage of reagents. The information provided therein is particularly appropriate to inorganic determinations. The type of volumetric glassware to be used, the effect of certain reagents on glassware, the effect of temperature on volumetric measurements, purity of reagents, absorption of gases and water vapor from the air, standardization of solutions, instability, and the need for frequent standardization of certain reagents are among the topics discussed. It is recommended that the analyst become thoroughly familiar with these publications.

5.2.1 General Inorganic Analyses

In general, AR-grade reagents and solvents are satisfactory for inorganic analyses. Primary standard reagents must, of course, be used for standardizing all volumetric solutions. Commercially prepared reagents and standard solutions are very convenient and may be used when it is demonstrated that they meet the method requirements. All prepared reagents must be checked for accuracy.

The individual methods specify the reagents that require frequent standardization, or other special treatment, and the analyst must follow through with these essential operations. To avoid waste, the analyst should prepare a limited volume of such reagents, depending on the quantity required over a given period of time. Examples and brief discussions of the kind of problems that occur are given in section 5.3.

As far as possible, distilled water used for preparation of reagent solutions must be free of measurable amounts of the constituent to be determined. Special requirements for distilled water are given in chapter 3 of this manual and in individual method descriptions.

Compressed gases, such as oxygen and nitrogen, used for total organic carbon determination may be of commercial grade.

5.2.2 Metals Analyses

All standards used for atomic absorption and emission spectroscopy should be of spectroquality. It is recommended that other reagents and solvents also be of spectroquality, although AR grade is sometimes satisfactory. Standards may be prepared by the analyst in the laboratory, or spectrographically standardized materials may be purchased commercially. Standards required for determination of metals in water are not generally available from the National Bureau of Standards.

Analytical-reagent-grade nitric and hydrochloric acids must be specially prepared by distillation in borosilicate glass and diluted with deionized distilled water. All other reagents and standards are also prepared in deionized water.

In general, fuel and oxidant gases used for atomic absorption can be of commercial grade. Air supplied by an ordinary laboratory compressor is quite satisfactory, if adequate pressure is maintained and necessary precautions are taken to filter oil, water, and possible trace metals from the line. For certain determinations such as aluminum, AR-grade nitrous oxide is required.

5.2.3 Radiological Analyses

The great sensitivity of radioactive counting instruments requires that scintillation-grade reagents and solvents, or equivalent, be used for all radioactivity determinations. Some of the reagents, for example, strontium carbonate and yttrium oxide carriers used for the determination of strontium-90 and yttrium-90, must be stable, that is, free of radioactivity. Barium sulfate, used for coprecipitation of radium, must be free from all traces of radium. These reagents and solvents are commercially available from chemical supply houses.

Calibrated standard sources of specific radioactive materials with known count and date of counting are available from various suppliers. No single company supplies all standards.

Gases used for radioactive counting must be of high purity and extra dry. Gases such as helium and air are aged for about 30 days to allow radioactive background to decay. All gases are checked for background before use. Some cylinders contain inherent radioactivity that is imparted to the gas. When this background is above normal, the gas should not be used for radioactivity determinations.

5.2.4 Organic Chemical Analyses

The minimum purity of reagents that can be used for organic analyses is AR grade. Reference-grade standards should be used whenever available. Special note should be taken of the assay of standard materials. Owing to the great sensitivity (nanogram and subnanogram quantities) of gas chromatography (GC), which is often used to quantitate organic results, much greater purity is frequently required (6). The specificity of some GC detectors requires that reagents and solvents be free of certain classes of compounds. For example, analyses by electron capture require that reagents and solvents be free of electronegative materials that would interfere with the determination of specific compounds in the sample. Similarly, use of the flame photometric detector requires that reagents and solvents be free from sulfur and phosphorus interference. Pesticide-quality solvents, available from several sources, are required when doing low-level work. AR-grade solvents are permissible when analyzing industrial waste samples.

However, the contents of each container must be checked to assure its suitability for the analyses. Similarly, all analytical reagents and other chemicals must also be checked routinely.

The quality of gases required for GC determinations varies somewhat with the type of detector. In general, the compressed gases are a prepurified dry grade. Grade A helium from the U.S. Bureau of Mines has always been satisfactory. The Dohrmann nitrogen detection system requires the use of ultrapure hydrogen for satisfactory results. Argon-methane used for electron-capture work should be oxygen free and should have an oxygen trap in the supply line. The use of molecular-sieve, carrier-gas filters and drying tubes is required on combustion gases and is recommended for use on all other gases. It is recommended that the analyst familiarize himself with an article by Burke (7) on practical aspects of GC.

All reagents, solvents, and adsorbents used for thin-layer chromatography must be checked to be certain that there are no impurities present that will react with the chromogenic reagent or otherwise interfere with subsequent qualitative or quantitative determinations. Glass-backed layers prepared in the laboratory or precoated layers supplied by a manufacturer may be used; however, precoated layers are more difficult to scrape. It is

recommended, therefore, that layers prepared in the laboratory be used when zones are to be scraped to recover isolated compounds. Plastic-backed layers are generally unsatisfactory for this type of analysis.

Adsorbents most commonly used for column chromatographic cleanup of sample extracts are Florisil,* silica gel, and alumina. These must be preactivated according to the method specifications and checked for interfering constituents.

5.3 Elimination of Determinate Errors

To produce high-quality analytical data, determinate errors must be eliminated or at least minimized. For purposes of this discussion, we assume that a competent analyst and reliable equipment in optimum operating condition are available. Thus, determinate errors that might result from an inexperienced or careless analyst and poor equipment are eliminated. The remaining sources of error are the reagents, solvents, and gases that are used throughout the analyses. The quality of these materials, even though they are AR grade or better, may vary from one source to another, from one lot to another, and even within the same lot. Therefore, the analyst must predetermine that all of these materials are free of interfering substances under the conditions of the analyses. To do this he must have a regular check program. Materials that do not meet requirements are replaced or purified so that they can be used.

5.3.1 Reagent Blank

The first step the analyst must take is to determine the background or blank of each of the reagents and solvents used in a given method of analysis. The conditions for determining the blank must be identical to those used throughout the analysis, including the detection system. If the reagents and solvents contain substances that interfere with a particular analysis, they should be treated so that they can be used, or satisfactory reagents and solvents must be found.

5.3.2 Method Blank

After determining the individual reagent or solvent blanks, the analyst must determine the method blank to see if the cumulative blank interferes with the analyses. The method blank is determined by following the procedure step by step, including all of the reagents and solvents, in the quantity required by the method. If the cumulative blank interferes with the determination, steps must be taken to eliminate or reduce the interference to a level that will permit this combination of solvents and reagents to be used. If the blank cannot be eliminated, the magnitude of the interference must be considered when calculating the concentration of specific constituents in the samples being analyzed.

A method blank should be determined whenever an analysis is made. The number of blanks to be run is determined by the method of analysis and the number of samples being analyzed at a given time. In some methods, such as the AutoAnalyzer procedures, the method blank is automatically and continuously compensated for because a continuous flow of the reagents passes through the detector. In other procedures, such as the gas chromatographic determination of pesticides, a method blank is run with each series of samples analyzed. Usually this is one blank for every nine samples.

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*Trademark of Floridin Co.

5.3.3 Elimination of Interferences and Other Sources of Error

Procedures for eliminating or at least minimizing impurities that produce specific interferences or high general background vary with the reagent and method involved. These procedures may include the following: recrystallization, precipitation, distillation, washing with an appropriate solvent, or a combination of these. Examples of procedures used for various types of analyses are given below. For complete information, the analyst should consult the individual methods.

5.3.3.1 General Inorganic Analyses

Analytical-reagent-grade chemicals and solvents usually present no interference problems in inorganic analyses. However, some reagents do not always meet methods requirements. An example is potassium persulfate used in phosphorus and nitrogen determinations. This reagent is frequently contaminated with ammonia. Therefore, it is routinely purified by passing air through a heated water solution of the reagent. The purified potassium persulfate is recovered by recrystallization.

A problem more commonly encountered in inorganic analyses is the rapid deterioration of the standard reagents and other ingredients. To minimize or eliminate this problem, some reagents, for example, ferrous ammonium sulfate, must be standardized daily. Others, such as sodium thiosulfate used for dissolved oxygen determination, may require a substitute reagent such as phenylarsine oxide. Solid phenol, which readily oxidizes and acquires a reddish color, can be purified by distillation. Starch indicator used for idiometric titrations may be prepared for each use or preserved by refrigeration or by addition of zinc chloride or other suitable compounds.

5.3.3.2 Metals Analyses

In general, spectrograde chemicals, solvents, and gases present no interference problems in atomic absorption or emission spectrographic determinations. However, standards that do not meet the requirements of the method are sometimes obtained. Ordinarily, no effort is made to purify them. They are simply replaced by new reagents of sufficient purity. Some reagents may form precipitates on standing. Such reagents will reduce the accuracy of quantitative analyses and should not be used.

5.3.3.3 Radiological Analyses

In general, reagents that do not meet the purity requirements for radiological determinations are replaced with reagents that are satisfactory. However, in some instances (for example, barium sulfate used for coprecipitation of radium) it may be necessary to perform repeated recrystallization to remove all forms of radium, and reduce the background count to a usable level. In some instances, solvents that do not meet requirements may be distilled to produce adequate purity. In some cases, gases having background counts may be usable after aging as described earlier. If not, they should be replaced with gases that are satisfactory.

5.3.3.4 Organic Analyses

Many AR-grade chemicals and solvents, and at times pesticide-quality solvents, do not meet the specifications required for the determination of specific organic compounds. Impurities

that are considered trace, or insignificant, for many analytical uses are often present in greater quantities than the organic constituents being measured. Coupled with the several-hundred-fold concentration of the sample extract that is usually required, such impurities can cause very significant interferences in trace organic analyses. Reagents and solvents found to be unsatisfactory, under the conditions of the analyses, must be replaced or cleaned up so that they are usable. Some useful cleanup procedures are—

a. Washing the inorganic reagents with each solvent that the reagent contacts during the analysis

b. Washing the adsorbents, such as silica gel G and Florisil, with the solvents that are used for a specified column or thin-layer chromatographic procedure, or reactivating the Florisil by firing to 630°C

c. Preextracting distilled water with solvents used for the particular analysis involved

d. Preextracting aqueous reagent solutions with the solvents involved

e. Redistilling solvents in all-glass systems using an efficient fractionating column

f. Recrystallizing reagents and dyes used in colorimetric or thin-layer determinations

If the reagents and solvents thus produced are not of sufficient purity, they should be replaced.

Dirty gases (quality less than specified) are particularly troublesome in gas chromatographic analyses. They may reduce the sensitivity of the detector, and produce a high or noisy baseline. If this occurs, the cylinder should be replaced immediately. Similarly, if cylinders of compressed gases are completely emptied in use, the end volumes of the gas may produce a similar and often more severe effect. Oils and water may get into the system and foul the detector. When this occurs the system must be dismantled and cleaned. Overhaul of the detector may be required. To reduce chances of this, it is recommended that all gas cylinders be replaced when the pressure falls to 100 to 200 psi. Filter driers are of little help in coping with this type of contamination.

5.3.4 Storing and Maintaining Quality of Reagents and Solvents

Having performed the tasks of selecting, preparing, and verifying the suitability of reagents, solvents, and gases, the analyst must properly store them to prevent contamination and deterioration prior to their use. Borosilicate glass bottles with ground-glass stoppers are recommended for most standard solutions and solvents. Plastic containers such as polyethylene are recommended for alkaline solutions. Plastic containers must not be used for reagents or solvents intended for organic analyses. However, plastic containers may be used for reagents not involved with organic analyses if they maintain a constant volume, and if it is demonstrated that they do not produce interferences and do not absorb constituents of interest. It is important that all containers be properly cleaned and stored prior to use. (Refer to ch. 4 for details.)

Standard reagents and solvents must always be stored according to the manufacturer's directions. Reagents or solvents that are sensitive to the light should be stored in dark bottles and in a cool, dark place. It is particularly important to store materials used for

radiological determinations in dark bottles, because photoluminescence will produce high background if light-sensitive detectors are used for counting. Some reagents require refrigeration.

Adsorbents for thin-layer and column chromatography are stored in the containers that they are supplied in, or according to the requirements of individual methods. When new stock solutions are necessary, dilutions of the old and new standard should be compared to determine their accuracy.

The analyst should pay particular attention to the stability of the standard reagents. Standards should not be kept longer than recommended by the manufacturer or in the method. Some standards are susceptible to changes in normality because of absorption of gases or water vapor from the air. Provisions for minimizing this effect are given in reference 4.

The concentration of the standards will change as a result of evaporation of solvent. This is especially true of standards prepared in volatile organic solvents. Therefore, the reagent bottles should be kept stoppered, except when actually in use. The chemical composition of certain standards may change on standing. Certain pesticides, for instance, will degrade if prepared in acetone that contains small quantities of water. Thus, it is essential that working standards be frequently checked to determine changes in concentration or composition. Stock solutions should be checked before preparing new working standards from them.

5.4 References

1. Catalog of Standard Reference Materials, NBS Special Publication 260, National Bureau of Standards (June 1975).
2. "Reagent Chemicals," American Chemical Society Specifications, 5th Edition, American Chemical Society, Washington, D.C. (1974).
3. Manual on Industrial Water and Industrial Waste Water, 2nd Edition, ASTM Special Publication 148-H, American Society for Testing and Materials (1965), p. 869.
4. "Standard Methods for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis," from Part 31 of 1976 Book of ASTM Standards, American Society for Testing and Materials, Philadelphia (1977).
5. Standard Methods for the Examination of Water and Wastewater, 13th Edition, American Public Health Association, New York (1971).
6. Methods for Organic Pesticides in Water and Wastewater, U.S. EPA, Environmental Research Center, Cincinnati (1971).
7. Burke, J., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," J. Assoc. Off. Anal. Chem., *48*, 1037 (1965).

Chapter 6

QUALITY CONTROL FOR ANALYTICAL PERFORMANCE

6.1 Introduction

Previous chapters discussed basic elements of quality control (QC) pertaining to laboratory services, instrumentation, glassware, reagents, solvents, and gases; the reader should refer to the appropriate sections to determine necessary specifications and requirements for QC. Assuming that these basic variables are under QC, that approved methods are being used, and that the complete system is initially under QC, valid precision and accuracy data must initially be developed for each method and analyst. Then, to insure that valid data continue to be produced, systematic daily checks must show that the test results remain reproducible, and that the methodology is actually measuring the quantity in each sample. In addition, QC must begin with sample collection and must not end until the resulting data have been reported. QC of analytical performance within the laboratory is thus but one vital link in the dissemination of valid data to the public. Understanding and conscientious use of QC among all field sampling personnel, analytical personnel, and management personnel is imperative. Technical approaches are discussed in the following sections.

6.2 The Industrial Approach to QC

In the 1920's, Dr. Walter A. Shewhart of Bell Telephone Laboratories, Inc. developed the theory of control charts as a basic method for evaluating the quality of products from manufacturing processes. His book (1) on statistical QC grew out of this original work. Later, acceptance of his concepts and related statistical techniques within industry led to refined, quantitative evaluations of product quality in manufacturing. Dr. Shewhart's work on production processes assumed a uniform product manufactured in large numbers and inspected on a continuous basis through the periodic analysis of samples of n production units. The resulting data, $x_1, x_2, \ldots x_n$, were then used to estimate precision, as the standard deviation S or range R, and accuracy, as the arithmetic mean $\bar{X}$. These statistics were calculated as follows:

$$S = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 / n}{n-1}}$$

R = the largest of the X_i - the smallest of the X_i

$$\bar{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

These statistics were evaluated by plotting them on control charts developed from similar statistics taken while the process was under properly controlled operation. The elements common to such control charts are represented in figure 6-1. They include an expected value (the central line) and an acceptable range of occurrence (the region between upper and lower control limits).

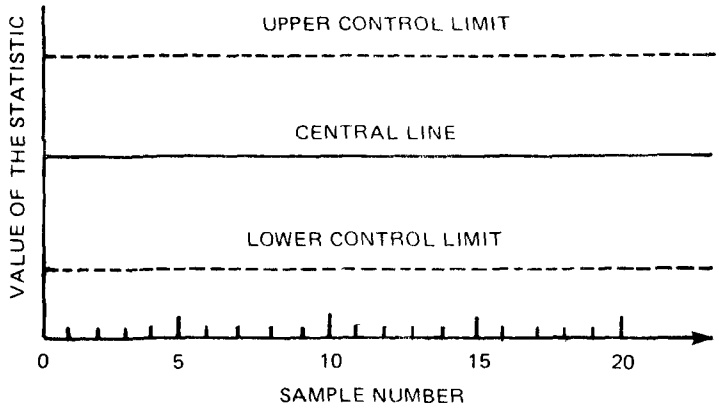

Figure 6-1. Essentials of a control chart.

There are many reference sources available that discuss in great detail the classic Shewhart control charts and related statistics that have since been developed for specific industrial applications (2-4). In addition, many authors have discussed applications of a related type of control chart called a cumulative-summation (cusum) chart (2,4). Rather than evaluating each sample independently, the cusum chart evaluates the cumulative trend of the statistics from a series of samples. Because each successive point is based upon a cumulative data trend, cusum charts are often considered more effective than control charts in recognizing process changes and, therefore, may minimize losses from production of unacceptable units; however, cusum charts require the more difficult calculations, and optimally designed Shewhart techniques have been found to be almost as effective (2,4), so there is no universal agreement on the choice between them.

6.3 Applying Control Charts in Environmental Laboratories

In industrial applications, separate control charts are recommended for each product, each machine, and each operator. Analogous system variables in an environmental laboratory are the parameter, the instrument, and the analyst. However, environmental laboratories routinely have to contend with a variable that has no industrial counterpart—the true concentration level of the investigated parameter, which may vary considerably among samples. Unfortunately, the statistics that work well for industry are sensitive to the variability in true concentration that is common in environmental analysis; e.g., the classic $\bar{X}$ and R statistic values increase substantially as concentration increases. This variability in true concentration means there are no expected values for randomly selected samples, so that the accuracy of testing methodology must be evaluated indirectly through the recovery of standards and spikes. As a result, it has been difficult for environmental laboratories to satisfactorily apply industrial QC techniques.

There are two possible approaches to the solution of the problem of variation in the true concentration level; either use of a statistic that is not sensitive to this variation or application of the industrial techniques within restricted concentration ranges. Obviously, the former should be preferred because it actually solves the problem and does not require the development and maintenance of a series of charts for each parameter.

6.3.1 Quality Control Charts for Accuracy

Two replacements for the Shewhart $\bar{X}$ control chart have been suggested for evaluating the recovery of a series of different standards or spikes. One of these, a cusum chart using the

square of the difference between the observed and true values, is described in an EPA Region VI QC manual (5). The other alternative uses the classic Shewhart technique to evaluate the percent recovery instead of $\bar{X}$. It is recommended that the percent recovery be calculated as

$$P = 100 \frac{\text{observed}}{\text{known}}$$

for standards, or

$$P = 100 \frac{\text{observed} - \text{background}}{\text{spike}}$$

for recovery of spikes into natural water backgrounds. An example of the linear relationship between percent recovery and the known concentration of standards and spikes is demonstrated in the accuracy plots of a recent EPA method study report on analysis of mercury (6). Both approaches are being used on a daily basis by various environmental laboratories.

The data in table 6-1 were used in the EPA Region VI manual (5) to illustrate the development of a cusum chart. The actual data have been reordered here to appear in ascending order of the known values. Note that the mean and the range of the d_i^2 values increase with increasing concentration level, and this violates a basic premise for acceptable control chart statistics. Because the percent recovery data do not show any such trend, it is the recommended control chart statistic for controlling accuracy.

From the data in table 6-1, a Shewhart control chart for percent recovery can be calculated in the following way:

Average percent recovery

$$\bar{P} = \frac{\sum_{i=1}^{23} P_i}{23}$$

$$= \frac{2,310}{23}$$

$$= 100.4$$

The standard deviation for percent recovery

$$S_P = \sqrt{\frac{\sum_{i=1}^{23} P_i^2 - \left(\sum_{i=1}^{23} P_i\right)^2 / 23}{22}}$$

$$= \sqrt{\frac{234{,}074 - (2{,}310)^2/23}{22}}$$

$$= \sqrt{94.0751}$$

$$= 9.70$$

Therefore, the upper control limit becomes the following:

$$UCL = \bar{P} + 3S_p$$

$$= 100.4 + 3(9.70)$$

$$= 129.5$$

Table 6-1
ANALYSIS[1] OF TOTAL PHOSPHATE-PHOSPHORUS STANDARDS, IN mg/l
TOTAL PO_4-P

Point	Known	Obtained	Difference d_i	d_i^2	Percent Recovery P_i	P_i^2
1	0.34	0.33	0.01	0.0001	97	9,409
2	0.34	0.34	0.00	0.0000	100	10,000
3	0.40	0.40	0.00	0.0000	100	10,000
4	0.49	0.49	0.00	0.0000	100	10,000
5	0.49	0.49	0.00	0.0000	100	10,000
6	0.49	0.63	-0.14	0.0196	129	16,641
7	0.50	0.47	0.03	0.0009	94	8,836
8	0.50	0.53	-0.03	0.0009	106	11,236
9	0.50	0.56	-0.06	0.0036	112	12,544
10	0.52	0.59	-0.07	0.0049	113	12,769
11	0.66	0.70	-0.04	0.0016	106	11,236
12	0.66	0.60	0.06	0.0036	91	8,281
13	0.67	0.65	0.02	0.0004	97	9,409
14	0.68	0.65	0.03	0.0009	96	9,216
15	0.83	0.80	0.03	0.0009	96	9,216
16	0.98	0.75	0.23	0.0529	77	5,929
17	1.3	1.2	0.10	0.0100	92	8,464
18	1.3	1.3	0.00	0.0000	100	10,000
19	1.6	1.7	-0.10	0.0100	106	11,236
20	2.3	2.3	0.00	0.0000	100	10,000
21	2.3	2.4	-0.10	0.0100	104	10,816
22	3.3	3.3	0.00	0.0000	100	10,000
23	4.9	4.6	0.30	0.0900	94	8,836
Totals					2,310	234,074

[1] Using a colorimetric method with persulfate digestion.

and the lower control limit becomes

$$LCL = 100.4 - 29.1$$

$$= 71.3$$

The completed control chart is shown in figure 6-2.

Following normal procedures, the control chart must indicate the conditions under which it was developed; i.e., laboratory name, parameter, method of analysis, date of preparation, and any other information unique to the initializing data, such as range of concentration and identification of analyst(s). A control chart is not generally applicable under other conditions.

To verify the control chart, the initializing data should be checked to be sure that none of the values exceeds these new control limits. In addition, if its distribution is proper, about 68 percent of the initializing data should fall within the interval $\bar{P} \pm S_P$. It has been suggested that the control chart is not valid if less than 50 percent of the initializing data falls within this interval.

In applying the control chart, either of the following two conditions would indicate an out-of-control situation:

a. Any point beyond the control limits

b. Seven successive points on the same side of the value $\bar{P}$ of the central line

When an out-of-control situation occurs, analyses must be stopped until the problem has been identified and resolved, after which the frequency should be increased for the next few percent-recovery QC checks. The problem and its solution must be documented, and all analyses since the last in-control point must be repeated or discarded.

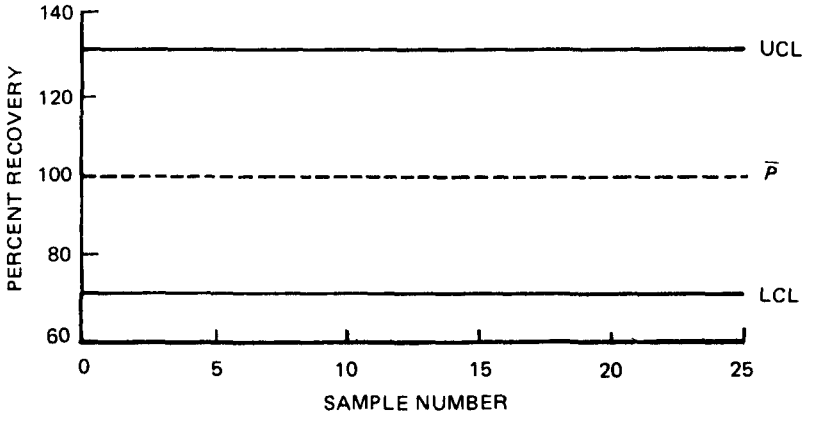

Figure 6-2. Shewhart control chart for percent recovery data.

A final note of caution regarding use of a single percent-recovery P control chart over a broad concentration range is necessary. As noted earlier for the analysis of mercury, a good linear relationship of the form

$$\bar{X} = P \text{ (known concentration)} + K$$

where K is a constant, seems appropriate for many parameters. However, to justify use of a single percent-recovery control chart, K must be small enough relative to the P(known concentration) term that it has little or no practical effect upon the value of $\bar{X}$. This will usually be true for moderate or high concentration levels, but may not be true at very low concentration levels. As a result, for some parameters it may be necessary to develop a separate percent-recovery or Shewhart $\bar{X}$ chart for each standardized low concentration level sample.

6.3.2 Quality Control Charts for Precision

Because the characteristics of the range statistic change as concentration changes, two alternatives to Shewhart's R chart have been used in environmental laboratories to evaluate the precision of routine sample analyses.

One alternative is a cusum chart using the sum of the squared difference between duplicate determinations on randomly selected routine samples (5). Because the range R for duplicate analyses is equal to the difference between them, the cusum statistic equals the sum of squared ranges $\sum R^2$. However, if R changes significantly as concentration level changes, then R^2 is affected even more and, therefore, is *not* as good a criterion for judging whether precision of the system is within acceptable limits.

The other alternative uses a chart similar to the R chart, but the chart statistic is either the percent relative standard deviation ($100S/\bar{X}$), the coefficient of variation (CV or $S/\bar{X}$), or the industrial statistic I. For the duplicate determinations A and B, I equals the absolute value of their difference divided by their sum, or $|A - B|/(A + B)$, and can be shown to be equivalent to the other two statistics:

$$100(\text{CV}) = 100\frac{S}{\bar{X}}$$

$$= 100\frac{R/\sqrt{2}}{(A+B)/2}$$

$$= 100\frac{2}{\sqrt{2}}\frac{R}{A+B}$$

$$= \frac{200}{\sqrt{2}}\frac{|A-B|}{A+B}$$

$$= \frac{200I}{\sqrt{2}}$$

For the sake of computational ease, I seems to be a logical alternative to R.

The next concern is whether I is independent of changes in concentration level. Based upon experience with duplicates on routine samples taken during the last 2 years by EPA Region VII, I appears to decrease substantially as concentration increases. In recognition of this possible dependency, control charts for I should only be developed from and applied to results within a limited concentration range. Note that control charts for R could be applied under similar limitations.

As an illustration of the concentration dependency of these precision statistics, table 6-2 provides estimates of R and I for different concentration ranges of three parameters. These parameters were selected because approximately 100 sets of duplicates were available that were well distributed over a reasonably broad concentration range. The ranges for the sum of duplicates $A + B$ used in table 6-2 were selected because they were convenient and the data tended to be well distributed among them. Data judged to be out of control were discarded before any calculations were made.

Table 6-2 indicates the concentration dependence of both the range R and the industrial statistic I for these three parameters. Because I is not independent of concentration and is

Table 6-2

ESTIMATES OF THE RANGE ($R = |A - B|$) AND THE INDUSTRIAL STATISTIC [$I = |A - B|/(A + B)$] OF THREE DIFFERENT PARAMETERS FOR VARIOUS CONCENTRATION RANGES[1]

Parameter	Range of $A + B$	No. of Sets of Duplicates	[2] $A + B$	[2] R	[2] I
BOD, 5-day (mg/l)	2 to <20	21	11.7	1.04	0.0888
	20 to <50	30	35.2	1.94	0.0552
	50 to <100	27	72.2	3.33	0.0462
	100 to <300	29	204.1	6.52	0.0319
	300 to <600	17	394.4	11.1	0.0282
	600 to <2,000	12	1,041	12.1	0.0116
	2,000 up	3	6,683	177	0.0264
Chromium (µg/l)	10 to <20	32	12.3	0.32	0.0306
	20 to <50	15	33.4	0.57	0.0170
	50 to <100	16	72.4	1.12	0.0155
	100 to <300	15	170.3	3.80	0.0223
	300 to <1,000	8	480.3	5.25	0.0109
	1,000 up	5	6,340	76.0	0.0120
Copper (µg/l)	10 to <30	16	22.2	0.93	0.0617
	30 to <50	23	38.2	1.35	0.0368
	50 to <100	21	70.8	1.14	0.0169
	100 to <200	26	131.9	2.33	0.0177
	200 to <400	10	268.0	2.81	0.0105
	400 up	3	702.0	4.56	0.0065

[1] From EPA Surveillance and Analysis Laboratory, Region VII.
[2] Average values.

Table 6-3
SHEWHART UPPER CONTROL LIMITS (UCL) AND CRITICAL RANGE R_c VALUES FOR THE DIFFERENCES BETWEEN DUPLICATE ANALYSES WITHIN SPECIFIC CONCENTRATION RANGES FOR THREE PARAMETERS[1]

Parameter	Concentration Range[2]	UCL	R_c
BOD, 5-day (mg/l)	1 to <10	3.40	3.5
	10 to <25	6.34	6
	25 to <50	10.9	11
	50 to <150	21.3	21
	150 to <300	36.3	36
	300 to <1,000	39.6	[3]40
	1,000 up	579	[3]579
Chromium (μg/l)	5 to <10	1.05	1
	10 to <25	1.86	2
	25 to <50	3.66	4
	50 to <150	12.4	12
	150 to <500	17.2	[3]17
	500 up	249	[3]249
Copper (μg/l)	5 to <15	3.04	3
	15 to <25	4.41	4
	25 to <50	3.73	5
	50 to <100	7.62	8
	100 to <200	9.19	[3]9
	200 up	14.9	[3]15

[1] From EPA Surveillance and Analysis Laboratory, Region VII.
[2] Equal to half of the range of $A + B$ given in table 6-2.
[3] Based on fewer than 15 sets of duplicate analyses.

more difficult to calculate and develop control charts for, the use of R charts for a series of sequential concentration ranges for each parameter seems practical. However, because the primary concern when using any range chart is whether the upper control limit has been exceeded, an even more practical approach would be to develop a table of these limits for all concentration levels of each parameter. As an example, table 6-3 contains the calculated Shewhart upper control limits for the range R from duplicate analyses within the various concentration levels for the three parameters in table 6-2. These limits were calculated, as usual, from the Shewhart factor D_4 for ranges based upon duplicate analyses and the appropriate average value of the range R given in table 6-2. For example, the UCL for 25 to 50 mg/l of BOD was calculated as follows:

$$\text{UCL} = D_4 R$$

$$= 3.27(3.33)$$

$$= 10.9$$

Table 6-3 also contains a critical range R_c column. Because the data from EPA Region VII were almost always whole units with only a very occasional half unit reported, the R_c value is the UCL value rounded to the nearest whole unit at higher concentration levels and to the nearest half unit for the lowest concentration level. However, there is an exception to this rule among the low-concentration R_c values for copper that demonstrates an advantage beyond the simplicity of using such tables. The UCL value for copper at 25 to 50 μg/l is inconsistent with the UCL values for adjacent concentration levels, and the R_c value has been adjusted to resolve this inconsistency. Without the table, such inconsistencies could very easily go unnoticed.

The examples in table 6-4 illustrate how to use the R_c values in table 6-3. This technique, consisting of the development and use of a table of critical-range R_c values at different concentration levels, is recommended to control precision. Normal control chart procedures should be followed as in section 6.3.1 regarding identification and verification of the table. The table should be updated periodically as additional, or more current, data become available, or whenever the basic analytical system undergoes a major change. If any difference between duplicate analyses exceeds the critical-range value for the appropriate concentration level, then analyses must be stopped until the problem is identified and resolved, and the frequency should be increased for the next few precision checks. After resolution, the problem and its solution must be documented, and all analyses since the last in-control check must be repeated or discarded.

6.4 Recommended Laboratory Quality Assurance Program

A minimum laboratory quality assurance program should include control procedures for each parameter as described in the following sections.

6.4.1 Standard Curves

A new standard curve should be established with each new batch of reagents, using at least seven concentration levels.

6.4.2 Quality Control Checks for Each Analytical Run

With each batch of analyses, the following tests should be run:

a. One blank on water and reagents

Table 6-4
CRITICAL RANGE VALUES FOR VARYING CONCENTRATION LEVELS

Parameter	Duplicates	R	R_c	$R \leqslant R_c$	Condition of System
BOD (mg/l)	20 and 24	4	6	Yes	Normal
Chromium (μg/l)	60 and 75	15	12	No	Out-of-control
Copper (μg/l)	46 and 51	5	[1]5	Yes	Normal

[1]This R_c value is used because (46 + 51)/2 = 48.5, which is between 25 and 50.

b. One midpoint standard

c. One spike to determine recovery

d. One set of duplicate analysis

The results from b through d should be compared with previous in-control data by using the appropriate technique recommended in section 6.3.

6.4.3 Interlaboratory QC

An interlaboratory QC program would require each laboratory to do the following:

a. Analyze reference-type samples to provide independent checks on the analytical system. These may be available from EPA as QC samples, from the National Bureau of Standards as standard reference materials, or from commercial sources. If performance limits are not provided, the results should fall within the routine limits of each laboratory for a standard at a level comparable to the specified true value.

b. Participate in performance evaluation and method studies as available from EPA, from the American Society for Testing and Materials, and from other agencies.

6.5 Outline of a Comprehensive Quality Assurance Program

In the following discussion the symbols used represent the results of analysis according to the scheme:

A_1 = first replicate of sample A

A_2 = second replicate of sample A

B = sample taken simultaneously with sample A

B_{SF} = field spike into sample B

B_{SL} = laboratory spike into sample B

D_F = field spike into distilled water

D_L = laboratory spike into distilled water

T = true value for all spikes

The laboratory spikes B_{SL} and D_L are the only analyses that may not be necessary. All other analyses *must* be done simultaneously.

6.5.1 Steps for the Field Personnel

A comprehensive quality assurance program would include the following steps for each parameter in the monitoring study:

a. Take independent simultaneous samples A and B at the same sampling point. Depending on the parameter, this might involve side-by-side grab samples or composite samplers mounted in parallel.

b. Split sample A into the equal-volume samples A_1 and A_2.

c. Split sample B into equal volumes and add a spike T to one of them; the latter sample becomes sample B_{SF}. As with all spikes, the addition of T should approximately double the anticipated concentration level.

d. Add the same spike T to a distilled water sample furnished by the laboratory and designate this sample as D_F.

These QC samples must be treated in the same way as routine samples; i.e., the volume, type of container, preservation, labeling, and transportation must be the same for all.

6.5.2 Steps for the Laboratory

The laboratory personnel should perform the following steps for quality assurance:

a. Analyze the blank and midpoint standard recommended in section 6.4. If results are unsatisfactory, resolve problems before continuing.

b. Analyze sample D_F. If the percent recovery of T is unsatisfactory (see section 6.3.1), create a similarly spiked, distilled-water sample D_L and analyze to test for a systematic error in the laboratory or fundamental problems with the spike. If the percent recovery of T from D_L is satisfactory, any systematic error occurred before the samples reached the laboratory.

c. Analyze samples B and B_{SF}. If B is below the detection limit, or if B is greater than $10T$ or less than $0.1T$, disregard the remainder of this step and proceed to step d. If the percent recovery of T from B_{SF} is unsatisfactory (see section 6.3.1), spike an aliquot of sample B the same way in the laboratory so that a similar recovery can be anticipated. Analyze this sample B_{SL} to test for immediate sample interferences or a bad background result B. If the percent recovery from B_{SL} is satisfactory, then the interference must require a longer delay before analysis, or other special conditions not present in the laboratory, in order to have a noticeable effect upon recovery of the spike.

d. Analyze A_1 and A_2. If the absolute (unsigned) difference between these results exceeds the critical value (see section 6.3.2), then precision is out of control.

e. Calculate the absolute difference between A_1 and B. If it is unsatisfactory (see section 6.3.2), the field sampling procedure did not provide representative samples.

If initial results at each of the laboratory steps were satisfactory, then the validity of the related data has been indisputably established. If results at any step are unsatisfactory, resolution depends upon the problem identified. Laboratory problems may just require that the analyses be repeated, but field problems will usually require new samples. Figure 6-3 is intended to clarify the interdependence of the preceding laboratory steps b through e.

In figure 6-3 it must be noted that there is no way to identify *additive* sample interferences; i.e., those that have an equal effect upon the background-plus-spike results (B_{SF} or B_{SL}) and the background result B. Recovery of a spike will not show such interferences.

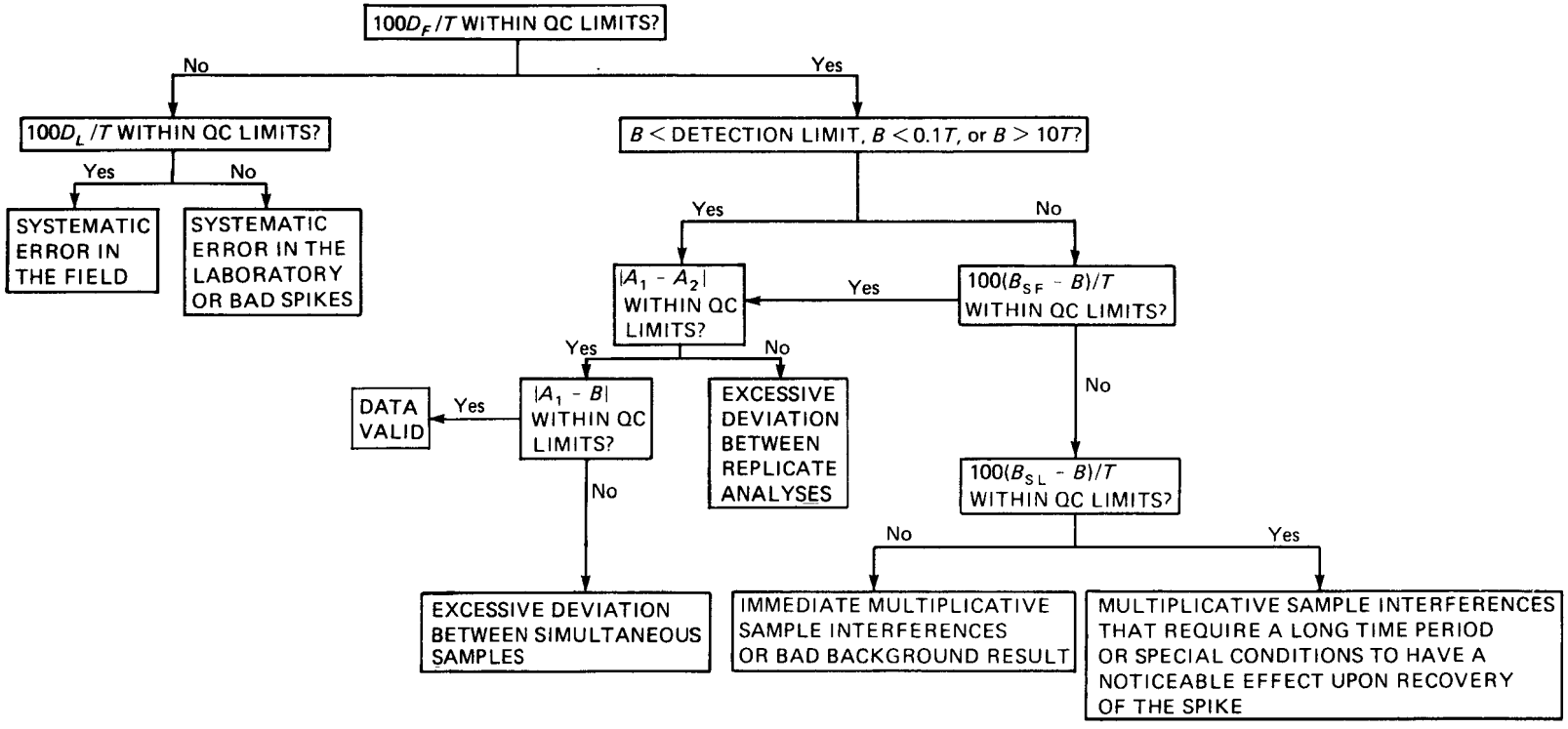

Figure 6-3. Procedure for evaluating QC data from a monitoring study.

Problems causing systematic errors that may occur in the field include the following:

a. Contaminated preservative, distilled water, or containers

b. Contamination by sampling personnel

c. Deterioration through excessive holding time or use of an ineffectual preservation technique

d. Use of a bad field-spiking procedure

6.6 Related Topics

6.6.1 Advanced Laboratory Automation and Its Effect on QC

Advanced laboratory automation systems under development analyze samples automatically and use a control computer to interpret the resulting data and produce an analytical report. The primary benefits of such a system are not only that the data-recording and calculation errors common to manual analyses have been inherently eliminated, but also that extensive QC can be accomplished quite easily and cheaply. The computer can be programed to automatically recognize different kinds of QC samples and to establish or recall appropriate control limits. Thus the QC overhead is reduced considerably and QC procedures previously too costly or complex become practical.

As an example of a QC procedure that is considered impractical for manual use, regression could be used to determine the relationship between concentration change and the accuracy and precision statistics discussed earlier. Using these relationships, very responsive, single accuracy and precision charts could be developed for each parameter. As computer-assisted analysis becomes common, automated laboratories will very likely replace the manual procedures recommended earlier in this chapter with evaluation criteria based upon regressions.

6.6.2 Method Comparability (Equivalency)

Requirements for method comparability are under development for proposed alternatives to the methodology specified in Public Law 92-500, section 304(g). A final version of these requirements should be available from EPA at a later date.

6.7 References

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5. Laboratory Quality Control Manual, 2d Edition, U.S. EPA, Region VI, Surveillance and Analysis Division, Ada, Okla. (1972).

6. Winter, J., Britton, P., Clements, H., and Kroner, R., "Total Mercury in Water," EPA Method Study 8, pp. 35-36, U.S. EPA, Office of Research and Development, EMSL, Cincinnati (Feb. 1977).

Chapter 7

DATA HANDLING AND REPORTING

7.1 Introduction

To obtain meaningful data on water quality, the sample collector must obtain a representative sample and then deliver it unchanged for analysis. The analyst must perform the proper analysis in the prescribed fashion, complete calculations, and convert results to final form for permanent recording of the analytical data in meaningful, exact terms. These results are transferred to a storage facility for future interpretation and use.

The following sections discuss processing of actual values, recording and reporting of data in the proper way, some means of quality control of data, and the storage and retrieval of data.

7.2 The Analytical Value

7.2.1 Significant Figures

The term "significant figure" is used, sometimes rather loosely, to describe a judgment of the reportable digits in a result. When the judgment is not soundly based, meaningful digits are lost or meaningless digits are reported. On the other hand, proper use of significant figures gives an indication of the reliability of the analytical method used.

The following discussion describes the process of retention of significant figures.

A number is an expression of quantity. A figure or digit is any of the characters 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, which, alone or in combination, serve to express a number. A significant figure is a digit that denotes the amount of the quantity in the particular decimal place in which it stands. Reported analytical values should contain only significant figures. A value is made up of significant figures when it contains all digits known to be true and one last digit in doubt. For example, if a value is reported as 18.8 mg/l, the 18 must be firm while the 0.8 is somewhat uncertain, but presumably better than one of the values 0.7 or 0.9 would be.

The number zero may or may not be a significant figure depending on the situation.

Final zeros after a decimal point are always meant to be significant figures. For example, to the nearest milligram, 9.8 g is reported as 9.800 g.

Zeros before a decimal point with nonzero digits preceding them are significant. With no preceding nonzero digit, a zero before the decimal point is not significant.

If there are no nonzero digits preceding a decimal point, the zeros after the decimal point but preceding other nonzero digits are not significant. These zeros only indicate the position of the decimal point.

Final zeros in a whole number may or may not be significant. In a conductivity measurement of 1,000 μmho/cm, there is no implication by convention that the conductivity is 1,000 ± 1 μmho. Rather, the zeros only indicate the magnitude of the number.

A good measure of the significance of one or more zeros interspersed in a number is to determine whether the zeros can be dropped by expressing the number in exponential form. If they can, the zeros may not be significant. For example, no zeros can be dropped when expressing a weight of 100.08 g in exponential form; therefore the zeros are significant. However, a weight of 0.0008 g can be expressed in exponential form as 8×10^{-4} g, so the zeros are not significant. Significant figures reflect the limits in accuracy of the particular method of analysis. It must be decided whether the number of significant digits obtained for resulting values is sufficient for interpretation purposes. If not, there is little that can be done within the limits of the given laboratory operations to improve these values. If more significant figures are needed, a further improvement in method or selection of another method will be required.

Once the number of significant figures obtainable from a type of analysis is established, data resulting from such analyses are reduced according to set rules for rounding off.

7.2.2 Rounding Off Numbers

Rounding off of numbers is a necessary operation in all analytical areas. It is automatically applied by the limits of measurement of every instrument and all glassware. However, when it is applied in chemical calculations incorrectly or prematurely, it can adversely affect the final results. Rounding off should be applied only as described in the following sections.

7.2.2.1 Rounding-Off Rules

If the figure following those to be retained is less than 5, the figure is dropped, and the retained figures are kept unchanged. As an example, 11.443 is rounded off to 11.44.

If the figure following those to be retained is greater than 5, the figure is dropped, and the last retained figure is raised by 1. As an example, 11.446 is rounded off to 11.45.

If the figure following those to be retained is 5, and if there are no figures other than zeros beyond the five, the figure 5 is dropped, and the last-place figure retained is increased by one if it is an odd number or it is kept unchanged if an even number. As an example, 11.435 is rounded off to 11.44, while 11.425 is rounded off to 11.42.

7.2.2.2 Rounding Off Arithmetic Operations

When a series of numbers is added, the sum should be rounded off to the same number of decimal places as the addend with the smallest number of places. However, the operation is completed with all decimal places intact, and rounding off is done afterward. As an example,

$$\begin{array}{r} 11.1 \\ 11.12 \\ +11.13 \\ \hline 33.35 \end{array}$$

The sum must be rounded off to 33.4.

When one number is subtracted from another, rounding off should be completed after the subtraction operation, to avoid possible invalidation of the operation.

When two numbers are to be multiplied, all digits are carried through the operation, then the product is rounded off to the number of significant digits of the multiplier with the fewer significant digits.

When two numbers are to be divided, the division is carried out on the two numbers using all digits. Then the quotient is rounded off to the number of significant digits of the divisor or dividend, whichever has the fewer.

When a number contains n significant digits, its root can be relied on for n digits, but its power can rarely be relied on for n digits.

7.2.2.3 Rounding Off the Results of a Series of Arithmetic Operations

The preceding rules for rounding off are reasonable for most calculations; however, when dealing with two nearly equal numbers, there is a danger of loss of all significance when applied to a series of computations that rely on a relatively small difference in two values. Examples are calculation of variance and standard deviation. The recommended procedure is to carry several extra figures through the calculations and then to round off the final answer to the proper number of significant figures.

7.3 Glossary of Statistical Terms

To clarify the meanings of statistical reports and evaluations of water quality data, the following statistical terms are introduced. They are derived in part from usage (1,2) of the American Society for Quality Control.

Accuracy—The difference between an average value and the true value when the latter is known or assumed.

Arithmetic mean—The arithmetic mean (or average) of a set of n values is the sum of the values divided by n:

$$\overline{X} = \frac{\sum_{i=1}^{n} X_i}{n}$$

Bias—A systematic error due to the experimental method that causes the measured values to deviate from the true value.

Confidence limit, 95 percent—The limits of the range of analytical values within which a single analysis will be included 95 percent of the time,

$$95 \text{ percent CL} = \overline{X} \pm 1.96S$$

where CL is the confidence level and S is the estimate of the standard deviation.

Constant—A nonvarying qualitative or quantitative characteristic of the population.

Geometric mean—A measure of central tendency for data from a positively skewed distribution (log normal),

$$\bar{X}_g = \sqrt[n]{(X_1)(X_2)\ldots(X_n)}$$

$$\bar{X}_g = \text{antilog}\ \frac{\sum_{i=1}^{n} \log X_i}{n}$$

Interference—A biological or chemical attribute of a test sample that positively or negatively offsets the measured result from the true value. If interference that is not segregated and identified is present, it enlarges or reduces the method bias.

Median—Middle value of all data ranked in ascending order. If there are two middle values, the median is the mean of these values.

n—The number of values X_i reported for a sample.

N—The total number of values X_i of the entire population or universal set of data.

Population—The total set of units, items, or measurements under consideration.

Precision—Relative to the data from a single test procedure, the degree of mutual agreement among individual measurements made under prescribed conditions.

Precision data—Factors that relate to the variations among the test results themselves; i.e., the scatter or dispersion of a series of test results, without assumption of any prior information.

Range—The difference between the highest and lowest values reported for a sample.

Relative deviation (coefficient of variation)—The ratio of the standard deviation S of a set of numbers to their mean $\bar{X}$ expressed as percent. It relates standard deviation (or precision) of a set of data to the size of the numbers:

$$\text{CV} = \text{RD (percent)} = 100\frac{S}{\bar{X}}$$

Relative error—The mean error of a series of measured data values as a percentage of the true value X_t,

$$\text{RE (percent)} = 100\frac{|X - \bar{X}|}{X_t}$$

Sample—Groups of units or portions of material, taken from a larger collection of units or quantity of material, that provide information to be used for judging the quality of the total collection or entire material as a basis for action on them or on their production processes.

Series—A number of test results with common properties that identify them uniquely.

Skewness—A measure of the asymmetry of a frequency distribution,

$$K = \frac{(X_i - \bar{X})^3}{n\sigma^3}$$

This measure is a pure signed number. If the data are perfectly symmetrical, the skewness is zero. If K is negative, the long tail of the distribution is to the left. If K is positive, the long tail extends to the right.

Standard deviation—The square root of the variance of the universe,

$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} X_i^2 - \left(\sum_{i=1}^{N} X_i\right)^2 / N}{N}}$$

Standard deviation estimate—The most widely used measure to describe the dispersion of a set of data. Normally $\bar{X} \pm S$ will include 68 percent, and $\bar{X} \pm 2S$ will include about 95 percent of the data from a study:

$$S = \sqrt{\frac{\sum_{i=1}^{n} X_i^2 - \left(\sum_{i=1}^{n} X_i\right)^2 / n}{n - 1}}$$

Standard deviation, single analyst—A measure of dispersion for data from a single analyst that is calculated here using an equation developed by Youden for his nonreplicate study design (3),

$$S_r = \sqrt{\frac{\sum_{i=1}^{n} (D_i - \bar{D})^2}{2(n - 1)}}$$

where D = the difference in paired values obtained from a single analyst.

Universe—The total set of items or measurements.

Variable—An experimentally determined estimate denoted X for a particular quality or trait of the population.

7.4 Report Forms

The analytical information reported should include the measured parameters; the details of the analysis such as burette readings, absorbance, wavelength, normalities of reagents, correction factors, blanks; and the reported data values.

To reduce errors in manipulation of numbers a general rule is to reduce handling and transposition of data to an absolute minimum. Ideally, a report form includes preliminary information about the sample and its analysis, and *the same* form is used for the final entering of data into a computer; however, such report forms are not yet common. Rather, a variety of methods is used to record data.

7.4.1 Loose Sheets

Reporting of data onto loose or ring-binder forms is a means of recording data that allows easy addition of new sheets, removal of older data, or collection of specific data segments. However, the easy facility for addition or removal also permits loss or misplacement of sheets, mixups in date sequence, and ultimately questionable status of the data for formal display or presentation as courtroom evidence.

7.4.2 Bound Books

The use of bound books is an improvement in data recording that tends to result in a chronological sequence of data insertion. Modification beyond a simple lined book improves its effectiveness with little additional effort. Numbering of pages encourages use of data in sequence and also aids in referencing data through a table of contents ordered according to time, type of analysis, kind of sample, and identity of analyst.

Validation can be easily accomplished by requiring the analyst to date and sign each analysis on the day completed. This validation can be strengthened further by providing space for the laboratory supervisor to witness the date and the completion of the analyses.

A further development of the bound notebook is the commercially available version designed for research-type work. These notebooks are preprinted with book and page numbers, and spaces for title of project, project number, analyst signature, witness signature, and dates. Each report sheet has a detachable duplicate sheet that allows up-to-date review by management without disruption of the notebook in the laboratory. The cost of research-type bound notebooks is about four times that of ordinary notebooks.*

Use of bound notebooks has been limited to research and development work where an analysis is part of a relatively long-term project, and where the recording in the notebook is the prime disposition of the data until an intermediate or final report is written.

However, bound notebooks can and should be used in routine analytical laboratories such as those concerned with water quality. The need for repeated information on sampling and analyses can be answered by use of preprinted pages in the bound notebooks.

7.4.3 Preprinted Report Forms

Most field laboratories and installations repetitively analyzing fixed parameters develop their own system of compiling laboratory data that may include bound notebooks, but a means of forwarding data is also required. Usually, laboratories design forms to fit a related group

*Scientific Notebook Co., 719 Wisconsin Ave., Oak Park, Ill. 60304.

of analyses or to report a single type of analysis for a series of samples. As much information as possible is preprinted to simplify use of the form. With loose-sheet, multicopy forms (using carbon or NCR paper) information can be forwarded on the desired schedule while also allowing retention of data in the laboratory. Still, the most common means for recording data in rough form are internal bench sheets or bound books. The bench sheet or book never leaves the laboratory but serves as the source of information for transfer of data to appropriate report forms. (See fig. 7-1.)

In most instances the supervisor and analyst wish to look at the data from a sampling point or station in relation to other sampling points or stations on a particular river or lake. This review of data by the supervisor prior to release is a very important part of the QC program of the laboratory; however, such reviews are not easily accomplished with bench sheets. For review purposes, a summary sheet can be prepared that displays a related group of analyses from a number of stations such as shown in figure 7-2. Because the form contains space for all of the information necessary for reporting data, the completed form can also be used to complete the data forms forwarded to the computer storage and retrieval system.

The forms used to report data to storage systems provide spaces for identification of the sampling point, the parameter code, the type of analysis used, and the reporting terminology. Failure to provide the correct information can result in rejection of the data, or insertion of the data into incorrect parameter fields. As sample analyses are completed, the data values are usually reported in floating decimal form along with the code numbers for identifying the parameter data fields and the sampling point data fields. Figure 7-3 shows an example of a preprinted report form used for forwarding data to keypunch.

7.4.4 Plastic-Coated Labels and Forms

A recent addition to good sample handling and data management is the availability of plastic-coated (blank or preprinted) labels, report forms, and bound report books. These materials are waterproof, do not disintegrate when wet or handled, can be written on while wet, and retain pencil or waterproof ink markings though handled when wet.

7.4.5 Digital Readout

Instrumental analyses, including automated, wet-chemistry instruments such as the Technicon AutoAnalyzer, the atomic absorption spectrophotometer, the pH meter, and the selective electrode meter, provide digital readout of concentrations, which can be recorded directly onto report sheets without further calculation. Programmed calculators can be used to construct best-fit curves, to perform regression analyses, and to perform series of calculations leading to final reported values.

7.4.6 Keypunch Cards and Paper Tape

Because much of the analytical data generated in laboratories is first recorded on bench sheets, then transferred to data report forms, keypunched, and manipulated on small terminal computers (or manipulated and stored in a larger data storage system), there is a danger of transfer error that increases with each data copy. The analyst can reduce this error by recording data directly from bench sheets onto punch cards that can be retained or forwarded immediately to the data storage system. Small hand-operated keypunch machines are available.

NL-C-88
(7-68)
Spectrographic Analyses Bench Data

Sample # ____ Date _____ Source _____ TDS _____

_____ ml. conc. to _____ ml. Factor _____

Test Count — Sec

1. _____ _____
2. _____ _____
3. _____ _____

	Count			Rerun Count			Av. Count	PPM In Conc. Sample	Less Than	(μg/l) PPB Orig. Sample
1. Zn									☐	☐☐☐☐
2. Cd									☐	☐☐☐☐
3. As									☐	☐☐☐☐
4. B									☐	☐☐☐☐
5. P									☐	☐☐☐☐
6. Fe									☐	☐☐☐☐
7. Mo									☐	☐☐☐☐
8. Mn									☐	☐☐☐☐
9. Al									☐	☐☐☐☐
10. Be									☐	☐☐☐☐
11. Cu									☐	☐☐☐☐
12. Ag									☐	☐☐☐☐
13. Ni									☐	☐☐☐☐
14. Co									☐	☐☐☐☐
15. Pb									☐	☐☐☐☐
16. Cr									☐	☐☐☐☐
17. V									☐	☐☐☐☐
18. Ba									☐	☐☐☐☐
19. Sr									☐	☐☐☐☐

Figure 7-1. Example of bench sheet.

MINERALS ANALYSES OF ZONE B, OHIO RIVER SAMPLES, CONC., mg/l.

STATION	Storet Number	Date	Alkalinity	Hardness	Chloride	Sulfate	Fluoride	SOLIDS		
								Total	Diss.	Susp.
Ohio at Ironton	200152									
Ohio at Greenup Dam	200001									
Ohio at Portsmouth	200139									
Scioto at Lucasville	381710									
Ohio at Maysville	200153									
Ohio at Meldahl Dam	383070									
Little Miami at Cincinnati	380090									
Ohio at Cincinnati	380037									
Licking at 12th Street	200523									
Ohio at Miami Fort	383072									
Ohio at Markland Dam	200521									
Kentucky at Dam 1	200522									
Ohio at Madison	174304									
Great Miami at Eldean										
Great Miami at Sellars Road	383047									
Great Miami at Liberty-Fairfield Road	383015									
Great Miami at American Materials Bridge	383007									
Whitewater at Suspension										
Great Miami at Lawrenceburg (Lost Bridge)	383071									

Figure 7-2. Example of summary data sheet.

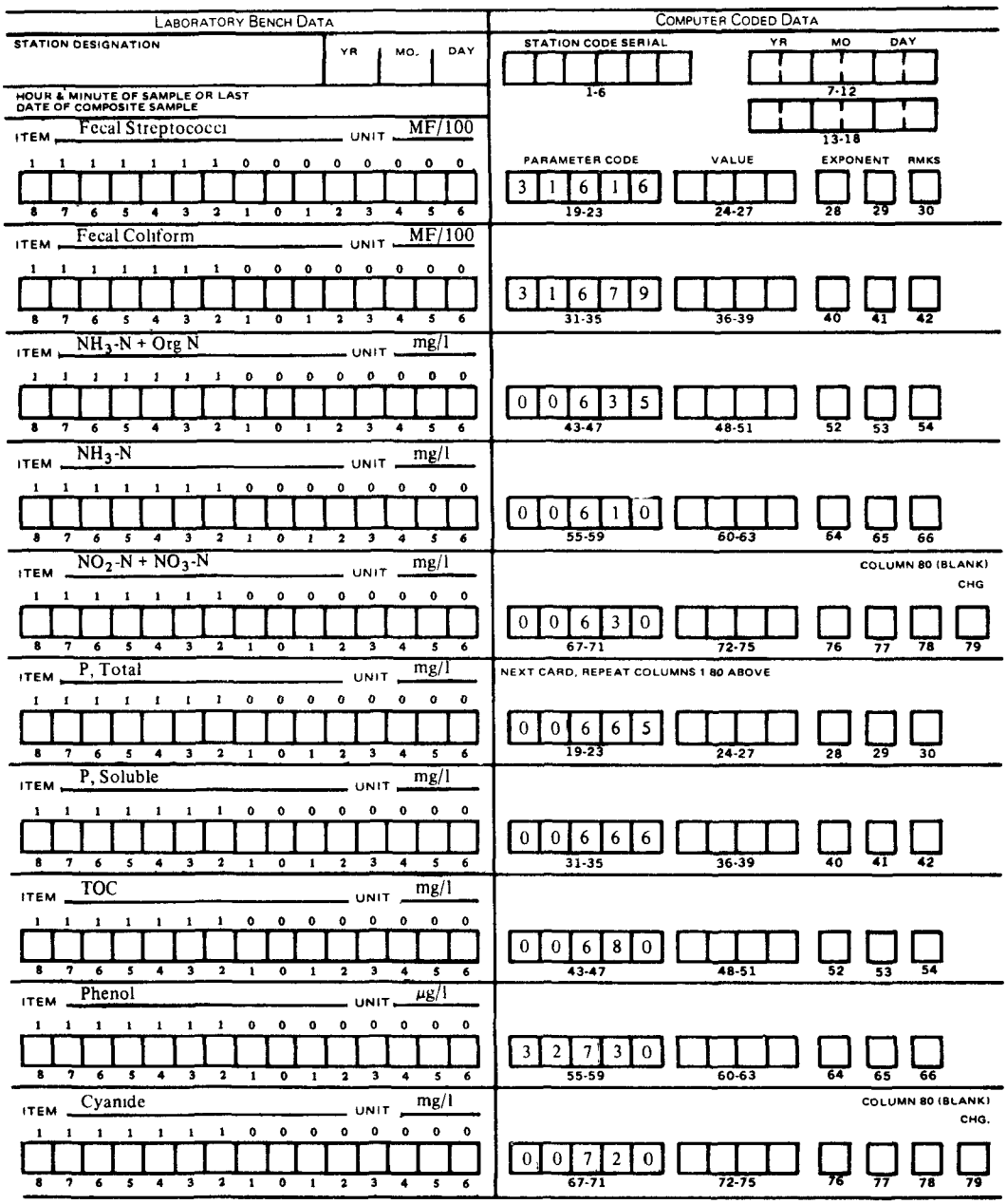

Figure 7-3. Example of STORET report form.

7.4.7 STORET–Computerized Storage and Retrieval of Water Quality Data

Because of their ability to record, store, retrieve, and manipulate huge amounts of data, the use of computers is a natural outgrowth of demands for meaningful interpretation of the great masses of data generated in almost all technical activities.

In August 1961, numerous ideas were brought together concerning the basic design of a system called STORET for storage and retrieval of water pollution control data. A

refinement of this system is now operated by the Technical Data and Information Branch, Division of Applied Technology, Office of Water Programs, EPA.

This is a State/Federal cooperative activity that provides State water pollution control agencies with direct, rapid access into a central computer system for the storage, retrieval, and analysis of water quality-control information.

If properly stored, the data can be retrieved according to such descriptors as the point of sampling, the date, and the specific parameters stored, or all data at a sample point or series of points can be extracted as a unit.

Full details on use of the STORET system are given in the recently revised STORET handbook (4).

7.4.8 Automated Laboratory Systems

The use of digital readout, keypunch cards, and paper tape have been overshadowed by the development of customized, fully automated online computer systems that make measurements, calculate results, perform quality control, and report analytical data simultaneously from a full range of laboratory instruments. (See fig. 7-4.) Such systems can contain the following functions:

a. Manual or automatic sampling and testing of a series of samples, standards, replicates, and check samples

b. Detection of the measurement signals from the series of samples

c. Conversion of signals to concentrations, generation of a standard curve, and calculation of sample values in final units

d. Calculation of the deviation and recovery values of the results and indication of acceptance or nonacceptance based on limits established by the analyst

e. Provision of the output in a form designated by the analyst: dial, paper recording chart, digital readout, cathode ray tube, or printed report form

The degree of hands-on operation required in the system is specified by the analyst.

If an automated system is properly designed and operated, most calculation and transposition errors are avoided and the proper level of quality control is automatically exerted. Laboratory automation systems for water analyses are being developed and coordinated by EMSL-Cincinnati for use in a number of EPA laboratories (5).

7.5 References

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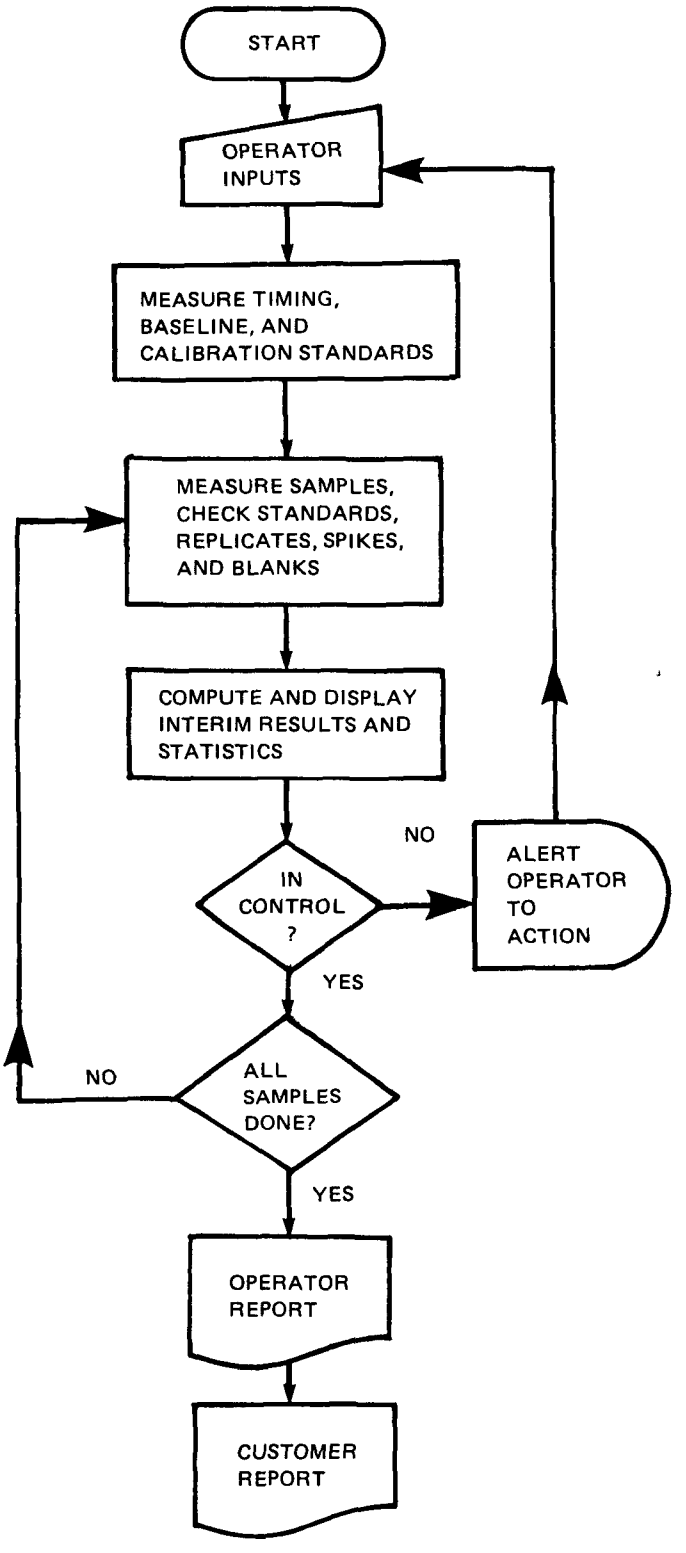

Figure 7-4. Flow chart of the sequence of events during a controlled series of laboratory measurements.

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Chapter 8

SPECIAL REQUIREMENTS FOR TRACE ORGANIC ANALYSIS

8.1 Introduction

The high sensitivity of the instrumentation used in trace organic chemical analysis and the low concentration of organic compounds being investigated dictate that special attention must be given to this analytical field. Contamination of the sample from any possible source must be diligently guarded against, and interferences in the sample must be carefully controlled. Strict attention to method and highly refined technique are required to produce valid quantitative and qualitative results.

Two manuals have been developed by the Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati covering the two broad areas of quantitative and qualitative trace organic analysis. Reference 1 contains both general and specific quality assurance programs designed to insure the production of acceptable measurements when using the methods contained in that manual. Reference 2 contains specific, detailed quality assurance programs covering both the performance of the instrument and the interpretation of the resulting spectra.

This chapter is organized with three sections devoted to general material applicable to all organic analysis, and one section abstracting highly specialized materials from each of the two manuals cited.

8.2 Sampling and Sample Handling

Regardless of the intent, all numbers generated by a water quality laboratory are ultimately represented as the concentration levels in the sample matrix at the time of collection. Such numbers tend, automatically, to endorse the sample collection, preservation, and shipment procedures. Thus, quality assurance programs limited to the care of the sample beginning with its receipt by the laboratory are inadequate. The laboratory must share responsibility for the preservation and shipment of all samples that it will accredit with concentration values. Two approaches are available that will generally protect the laboratory from generating numbers that may not reflect actual conditions of the sample at the time of collection. The best, but usually least practical solution, is for the laboratory personnel to collect all samples. The alternative is for the laboratory to adopt a policy of sample rejection based on minimum standards of sample identification and age. Guidelines for establishing these standards are discussed in this section. It is recommended that copies of this material be supplied to all sample collectors along with an understanding of the specific policy of the laboratory toward rejecting samples that do not meet these criteria.

In all of the cases to be discussed, it is the responsibility of the project director to (a) coordinate his sampling, preservation, and shipment with the laboratory, (b) obtain clean sample containers from the laboratory, (c) provide adequate sample identification and compositing instructions, and (d) provide duplicates and blanks as required by the laboratory. Additional prearrangements should be made with the laboratory if sample splitting is desired, to create separate supernatant and settleable matter samples, or if calculations on a wet-weight basis in addition to the standard dry-weight calculations are desired.

Bottles and caps are to be supplied by the laboratory because rigorous cleaning is required even for new bottles. New and recycled bottles should be washed as described in reference 1. Samples received in bottles of unknown origin or questionable cleanliness should be rejected by the laboratory. For water samples that are to be analyzed by solvent extraction methods, narrow-mouthed, screw-cap bottles such as Boston rounds are preferred because they have less tendency to leak and are easy to handle in the laboratory. One-liter bottles are generally more expensive than quart bottles, thus most laboratories use the clear 32-oz containers. The bottle should be sealed with Teflon (du Pont) lined caps. For water samples of intermediate pH, aluminum-foil-lined caps may be used when Teflon (du Pont) is not available. Oil and grease samples can be collected with Polyseal caps—the conical liner provides an excellent seal against pressure during shipment and sample extraction. Screw-cap, widemouthed glass bottles are preferred for sediment samples because they are easier to handle in the field and in the laboratory. Precleaned, 16- or 32-oz bottles with Teflon (du Pont) or foil-lined screw-cap closures should be provided by the laboratory. Masking tape or other suitable labels should be applied to the dry bottles.

Sampling for purgeable organics requires special consideration and equipment. The sample container should consist of a 45-ml, screw-cap vial fitted with a Teflon (du Pont) faced, silicone septum.* The vials, septa, and caps should be washed in hot detergent water and thoroughly rinsed with tapwater and organic-free water, then dried at 105°C for 1 h. The vials should then be cooled to room temperature in a contaminant-free area. When cool, the vials should be sealed with the septa, Teflon (du Pont) side down, and screw cap and maintained in this sealed condition until filled with sample.

The bottles used for collecting water samples for solvent extraction should not be overfilled or prerinsed with sample before filling because oil and other material that can cause erroneously high results may remain in the sample bottle after rinsing. Bottles should be filled with sample to about 90 percent of capacity, and the level should be marked to determine if leakage occurs. Because full sample bottles are difficult to pour from during extractions, complete filling should be avoided. In the collection of sediment samples, nonrepresentative debris such as large stones or wood should be discarded.

Multiple samples are usually required for purgeable organics analysis because of leakage and because the measurement process is destructive to the sample. All vials should be identified with waterproof labels. The water sample vials are filled to overflowing from a bubble-free source so that a convex meniscus is formed at the top. They are sealed by carefully placing the septum, Teflon (du Pont) side down on the opening of the vial and screwing the cap firmly in place.

Shipment and receipt of samples must be coordinated with the laboratory to minimize time in transit because it is the prerogative of the laboratory to reject samples where delays in shipment have caused them to age beyond acceptable holding times. To avoid the need to resample, the sampler should determine in advance the most efficient and reliable form of transportation for the samples. All samples for organic analysis should arrive at the laboratory on the same day collected, or should be shipped and maintained at less than 4°C for arrival by the next day. The samples are usually shipped in insulated ice chests. Water samples should be prechilled before packing to reduce the ice requirements during shipment.

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*Vial and septum are available from Pierce Chemical Co., P.O. Box 117, Rockford, Ill. 61105. Vial: No. 13074; septum: No. 12722.

The bottles should be stabilized in the container with styrofoam and covered with ice. The information needed to identify the samples should be attached to the outside of the ice chest.

A part of the quality assurance program for a laboratory must be the development of a clear policy for accepting or rejecting samples. Because organic analyses are expensive in terms of manpower and supplies, it is poor management to commit such resources just to obtain data of questionable validity. Water samples that clearly have not met the preservation criteria during shipment (e.g., in the case of a spill) should be accepted only if resampling is impossible. Results from such samples must be qualified in the laboratory report.

Upon receipt, the samples should be checked for adequate identification, sample temperature or presence of ice in the chest, and leakage. Samples for volatile organics should be checked for air bubbles, although it is extremely difficult to avoid the development of very small bubbles regardless of the type of sample bottle employed. The samples are logged in with the receipt time noted. Unless the condition of the samples fails to meet the criteria for acceptance by the laboratory, required preservatives are added immediately and the samples are all refrigerated.

The laboratory staff should be alerted to the arrival of the samples, so that the required analysis can begin as soon as possible. When sediment samples are to be reported on a wet-weight basis, or when a water sample is to be filtered or divided into supernatant and settleable subsamples for separate analysis, the sample processing should begin promptly.

When analysis of water samples is to be restricted to the water phase only, filtration is required. This may be accomplished with 4.7-cm, glass-fiber filter disks that have been preextracted with acetone and allowed to dry. The filter disks must not contain organic binder. The disks are placed on a membrane filter holder and up to a liter of water is filtered. The filtrate is transferred without rinsing to a clean sample container and treated as a normal, whole-water sample.

When separate reporting is required for the settleable and supernatant phases, the water sample (or a large portion of it) is allowed to settle overnight in a closed glass container at 4°C. If phase separation occurs, the supernatant phase is carefully decanted or siphoned into a graduated cylinder without disturbing the surface of the settled material. After the volume of supernatant is noted, the supernatant is filtered as just described into a clean glass container and stored at 4°C. The volume of settled material is determined either by marking the slurry level on the side of the sample container for later calibration, or by transferring the slurry without washing into a calibrated vessel. A portion of well-mixed slurry is removed for a determination of percent solids. The remaining slurry is stored in a sealed glass container at 4°C.

When both dry-weight and wet-weight results are required for sediments and sludges, a percent-solids determination should be performed soon after receipt of the sample. A representative portion (ideally 10 to 25 g) of well-mixed sample is weighed into a tared Erlenmeyer flask and dried at 105°C to a constant weight. Then percent solids are calculated for the sample.

Routine laboratory management involves detailed recordkeeping beginning with the initial contact with the sample collector. A master flowsheet should be prepared for each sample, listing parameters to be determined and pretreatment operations to be performed. The

master flowsheet is kept at a fixed location and is designed to handle dated entries indicating when operations are completed. Methods requiring extraction permit double entry on the master flowsheet so laboratory throughput times can be calculated in terms of receipt-to-extraction and receipt-to-completion times. A separate set of forms follows the sample through the laboratory. Each sample form records information for a class of parameters and details cleanup operations and other method options. Calculations and cross references to chromatograph files are entered on the sample form also.

A chain-of-custody program lends significant legal support to the results generated. The program begins when the laboratory dispatches the sample collectors. Each time a sample is collected, a form is initiated stating where and when the sample was collected, with cross reference to a number on the sample container. The sample collectors return to the laboratory with the samples in their guarded possession and deliver them personally to the responsible person in the laboratory. The person (custodian) receiving the samples in turn signs each ledger to acknowledge receipt and locks the sample in a refrigerator. The analyst then comes to the custodian and signs for the sample that he is taking for analysis. In this way full documentation of the sample handling is maintained from sample collection through completion of the analysis.

8.3 Extract Handling

Each method in reference 1 is prepared in sections identified by titles. This style of presentation is aimed at presenting the analyst logical places to interrupt his analysis. Often, because of the length of the method, the analyst is unable to complete an analysis in a single day. When planning a partial analysis, certain factors must be considered. Because the organics are generally more stable in solvent than in water, it is always preferable to extract a sample and hold the extract rather than to hold the sample. Extracts to be held overnight or longer should first be dried by treatment with sodium sulfate.

The methods include several transfers of the solvent extract from one piece of glassware to another. These quantitative transfers are made using several small portions of solvent to wash the walls of the previous container. A 5-ml, luer-lock glass syringe with a 2-in., 20-gage needle is convenient for this purpose. Solvents tend to creep up the outside of a container, such as an ampoule, while pouring. To minimize contamination during transfer, solvent extracts are poured as rapidly as possible. Extracts can become contaminated not only from oils from the skin of the handler but also from other extracts handled at the same time where deposits on the outside of the container are unintentionally transferred from one container to another. Instead of using labels, contamination problems from this source can be reduced by etching permanent numbers on ampoules. Sample log sheets should be used to index the extract with a numbered ampoule, eliminating the need for tape or wax pencils.

Of the several ways to dry a solvent extract with sodium sulfate, passing it through a chromatographic column packed with 2 to 3 in. of anhydrous crystals is the most convenient and quantitative. When a wet extract is being transferred from a separatory funnel to a Kuderna-Danish (K-D) concentrator, it should be drained directly through the column to eliminate the need for an intermediate piece of glassware and the resulting transfer step. Prewashing the sodium sulfate column with extracting solvent is recommended, although interferences can be controlled by preheating the salt in a shallow tray at 400°C for 30 min. After the extract has passed through the column, 20 to 30 ml of extracting solvent are used to wash the residual extract from the column.

The standard K-D concentration apparatus consists of a three-ball Snyder column, a 500-ml flask, and a calibrated ampoule. It is designed to concentrate 100- to 300-ml volumes of extract to a final volume of 5 to 10 ml. To use the apparatus, one 10/20 mesh boiling chip (previously rinsed with solvent and heated for 1/2 h) is added, and the assembly is supported above a concentric-ring water bath with the tip of the ampoule below the surface of the water. The lower ground-glass joint must be kept above the water. The water temperature should be adjusted for mild distillation, with no chamber flooding or splashing (about 10°C to 20°C above the boiling point of the solvent). When the volume of liquid reaches 1 to 2 ml (checked frequently), the assembly should be removed and allowed to cool. The chambers and flask will drain to a final volume near 10 ml. The flask and the lower ground-glass joint are rinsed with a minimum of solvent. The evaporation can be continued with the microscale K-D concentrator if further concentration is required.

The microscale K-D concentrator is designed to concentrate extracts from 5 to 10 ml to 1.0 ml. A fresh boiling chip must be added, and a two-ball micro-Snyder column is attached to the ampoule. The ampoule is supported above the water bath, and the extract is concentrated to about 0.7 ml. The column and ground-glass joint are rinsed with a minimum of solvent, and the volume is adjusted to 1.0 ml.

The K-D concentrator can be used to exchange solvents. When the sample is dissolved in a solvent unsuitable for a cleanup operation or for gas chromatography (GC), it can be displaced by a suitable higher boiling solvent. The actual volumes that should be used to effect the exchange vary with the solvent pairs depending upon the difference in boiling points and azeotrope formations, but a general procedure is to concentrate the extract to 10 ml, add 20 ml of the higher boiling solvent, and reconcentrate to 10 ml.

After extractions and subsequent K-D concentrations, solubilities of some materials may be exceeded. High sulfur levels are a particular problem encountered in sediment extractions. Extracts should be decanted from ampoules where sulfur has crystallized. In some samples the extractable organic levels are so high the extract tends to solidify and will not concentrate further. When this occurs, a small aliquot of the extract should be taken and diluted as appropriate for final analysis.

A significant source of the variation in GC analysis can be attributed to the injection of a portion of the extract into the analytical system. Manual injections of 2 to 3 μl with the use of a 10-μl syringe will introduce variance even when the injection volumes are determined to the nearest 0.05 μl. Of a variety of injection techniques in use, the solvent flush technique has been found to be acceptable for quantitative work. This technique is described in detail in reference 1.

8.4 Supplies and Reagents

Reference compounds of materials should be assayed and of 98 percent purity or higher. If the purity is less than 98 percent, the appropriate correction factor must be included in all calculations of standard concentration. The reference materials should be cataloged, dated, and stored in a refrigerator.

Stock solutions of these reference materials should be prepared in a high-boiling, inert solvent, if possible, to minimize errors due to evaporation or solvent-induced decomposi-

tion. The laboratory should have an accurate six-place balance for preparing small quantities of reference standards. The following method of preparing stock solutions is recommended: Weigh 10 mg (to the nearest 0.01 mg) of reference standard into a small aluminum weighing pan.* Drop the entire pan into a 10-ml volumetric flask. Dissolve the reference material in about 5 ml of solvent, then dilute to volume. Label the solution with compound name, concentration, solvent used, date prepared, and initials of preparer. Store the volumetric in a refrigerator, except when preparing dilutions. When the standard is a replacement for an existing stock solution, the two solutions should be compared, and the results as well as the suspected reason for any variation should be permanently recorded in the laboratory files.

Working standards are prepared from one or more stock solutions after they have warmed to room temperature. As these working standards usually represent three to six orders of magnitude of dilution of the stock standards, it is obviously necessary to take great care in preparing them. Serial dilutions are recommended with a maximum of 1:100 dilution for each step. Although 10-μl volumes can be read within 1 percent with a 10-μl syringe, the inherent problems with the dead volume in the syringe make the use of such equipment less desirable for preparing working standards than volumetric pipets. New working standards should be prepared frequently unless long-term stability has been demonstrated. When several compounds are combined into a single standard for simultaneous GC, they must be closely monitored for chemical interactions.

Pesticide-quality solvents are usually required, and each new lot should be checked for interferences prior to use. The solvent check, representing approximately 10 percent more solvent than required for any method, should be concentrated and analyzed for method interferences under all GC conditions applicable to that solvent. If interfering peaks or a broad solvent front are observed, the solvent should be redistilled in an all-glass distillation system, with a distillation column.** If interferences persist, the solvent lot should be discarded. This preliminary lot check does not eliminate the need for routine solvent blanks to monitor for purity changes over a period of time.

Diethyl ether must be shown to be free of peroxides before use. Peroxide test strips† can be used for a quick, convenient test. The alumina column procedure for removing peroxides, described in literature supplied with the test strips, has been used successfully to remove all peroxides from the solvent. The solvent should always be stabilized with 2 percent volume/volume ethyl alcohol. Chromatographic elution patterns are based on ether containing this alcohol.

Granular sodium sulfate should be purchased in glass containers. If purchased in a large container (5-lb bottles or larger), it should be transferred to smaller bottles for daily use. Before sodium sulfate is used for chromatographic work, it should be heated to 400°C for 30 min and shown not to be contaminated. When the sodium sulfate is used to dry extracts before concentration, the heating is usually unnecessary because impurities will be removed by preelution of the drying column with solvent.

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*Available from The Perkin-Elmer Corp., Norwalk, Conn.; No. 219-0041.

**Available from Lab Glass, Inc., North West Blvd., Vineland, N.J. 08360; Widner No. LG-5930.

†Available from Scientific Products, 1430 Waukegan Rd., McGaw Park, Ill. 60085; Quant peroxide test strip, No. P1126-8.

Florisil (Floridin Co.) is purchased from the manufacturer preactivated at 630°C and transferred to glass containers with Teflon (du Pont) or foil-lined lids. Prior to use the Florisil (Floridin Co.) is heated in a shallow open dish for 5 h in a 130°C oven. The Florisil (Floridin Co.) can then be transferred into a sealed, glass bottle and stored indefinitely at 130°C until needed. Cleanup methods using Florisil (Floridin Co.) require that a lauric acid value be determined for each lot before use. In addition, the determination of a pesticide elution pattern is recommended. These procedures are described in detail in reference 1.

Carrier gases are a very important part of the chromatographic system; therefore, special care should be taken in their selection and handling. Only high-purity or equivalent carrier gases should be purchased, and they should be filtered, online, through a 5-Å molecular sieve. Porous polymer and other column packings degrade at elevated temperatures in the presence of trace quantities of oxygen. Oxygen in the carrier gas also adversely affects the performance of electron-capture detectors. Therefore, some type of online oxygen-removal system is recommended for these applications. The chemical traps should be changed or regenerated with each new cylinder of carrier gas. One purifier* has been found to last through many cylinders without replacement. A better grade of gas is required for temperature programing than for isothermal operation. Combustion gases may be of lower quality but should be at least equivalent to dry air or purified hydrogen. Regulators should have stainless steel internal parts and be of two-stage design. External tubing should be of good quality, such as refrigeration tubing. Such tubing should be rinsed with solvent and heated at 200°C under gas flow before use in the analytical system.

The purchase of precoated GC column packings is strongly recommended over the preparation of coated materials in the laboratory. The commercial products are, generally, of higher quality and consistency than those prepared by the average analyst. All tubing should be cleaned before packing by passing a series of solvents (e.g., hexane, chloroform, and acetone) through it. Glass columns should also be silylated. (Instructions are included with the purchase of silylating agents.) Dry the tubing thoroughly before packing it.

A vibrator should never be used to settle the packing material in the column. Such vibration may fracture the solid support material, expose uncoated active sites, and produce inferior chromatographic separations. When vacuum alone is inadequate and further settling is required, the column may be tapped with a pencil or similar object while the vacuum is being applied. Unless otherwise stated, stainless-steel tubing should be packed before coiling it to fit the GC apparatus.

8.5 Quality Assurance

8.5.1 Measurements

Most of the quality assurance programs suggested in chapter 6 of this manual cannot easily be adapted to the methods for organic compounds. The reasons for this, and the suggested approach for a suitable program for the organic analytical laboratory are discussed in detail in reference 1 and only summarized here.

Reference 1 suggests that quality assurance for organic analysis be divided into three separate categories. The first category represents the determination of purgeable com-

*Available from Matheson Gas Products, P.O. Box E, Lyndhurst, N.J. 07071; Hydrox Purifier model No. 8301.

pounds. This determination is performed in a closed analytical system; the complete analysis can be performed in 1 h; and the number of theoretically possible interferences is somewhat limited. The second category represents liquid/liquid partition methods in a regulatory situation. Here a very limited number of compounds are being measured; there is a high occurrence of positive results; and it is important to establish that the method works satisfactorily on the particular sample matrix. The third category represents liquid/liquid partition methods in a monitoring situation. Here a large number of compounds are often being measured simultaneously; there is a low occurrence of positive results; and each sample matrix may be different. Quality assurance is aimed at establishing that the laboratory is using the method correctly.

The purgeable methods are unique among organic methods because the standards are treated in exactly the same way as the samples, and there is no inherent method bias. The methods are amenable to a variety of quality assurance programs. The approach that has been found applicable to all types of samples and provides the maximum data for the expended effort consists of the addition of one or more internal standards to the matrix before purging. Data generated in this program provide a continuous monitoring of the equipment and establishes matrix applicability for the test.

For liquid/liquid extraction methods in a regulatory situation, the emphasis is placed on duplicates and dosed samples. Both field duplicates and laboratory duplicates are used in the program to establish sampling and subsampling validity. The dosing of samples to establish method accuracy for the matrix is an integral part of this program. Where the analytical program will extend over a long period of time the construction of control charts is recommended.

When the liquid/liquid extraction methods are used for monitoring, the emphasis is placed on an external control series. A standard laboratory matrix is developed. With each series of samples the matrix is dosed and analyzed with the samples. Data generated over a period of time can be used to monitor the performance of the equipment and the analyst, with relatively tight specifications to define problems that arise. Control charts can be constructed to alert the analyst to problems, but there is no provision for rejection of results for samples of this type.

8.5.2 Identifications

The combined gas chromatography/mass spectrometer (GC/MS) has emerged as the most important single instrument at the disposal of the environmental analytical chemist. It alone can provide both the sensitivity and the high degree of certainty necessary for an identification culled from a complex environmental matrix. The instrument has generated an aura of well-deserved respect, and its results are seldom questioned. For these reasons it is mandatory that strict quality assurance programs be followed in both the generation and the interpretation of mass spectra. The EMSL, with the cooperation of many other EPA GC/MS users, has produced a procedural manual (2) generally for use with a Finnigan quadrupole instrument. A detailed quality assurance program constitutes an integral part of the manual. The actual detailed program is beyond the scope of this manual but has been summarized in the following paragraphs.

To insure that a quadrupole mass spectrometer generates quality spectra, the program provides for at least daily performance evaluation with a reference compound, and

readjustment of the instrument as necessary. The operator prepares a solution of decafluorotriphenylphosphine (DFTPP).* When this compound is injected into the GC/MS using any of several compatible GC columns, the resulting elaborate spectrum can be evaluated using criteria developed at EMSL-Cincinnati (3).

Decafluorotriphenylphosphine key ions and the ion-abundance criteria that are used for determining whether the mass spectrometer is generating high-quality spectra are as follows:

Abundance Criteria

Mass (amu)	*Ion Abundance Criteria*
51	30 to 60 percent of mass 198
68	Less than 2 percent of mass 69
70	Less than 2 percent of mass 69
127	40 to 60 percent of mass 198
197	Less than 1 percent of mass 198
198	Base peak, 100 percent relative abundance
199	5 to 9 percent of mass 198
275	10 to 30 percent of mass 198
365	1 percent (or greater) of mass 198
441	Less than mass 443
442	Greater than 40 percent of mass 198
443	17 to 23 percent of mass 442

If these specifications are not met, the guidelines provided for adjusting the instrument (2,3) must be considered.

Having produced quality spectra, the analyst must always ascertain, by analyzing a method blank under exactly the same analytical and instrumental conditions, that the spectra are relevant. Most commercial systems have a software program, extracted ion current profile (EICP), that permits the sample and the blank to be overlayed on a graphic display device when each is scanned for a particular mass. When large numbers of spectra result from a sample and the blank must be checked for a match for each one, this technique simplifies the screening process.

If the spectra are found to be unique to the sample, it is normally processed through a mass-spectral search-and-match system. The computerized version of such a system consists

*Available from PCR Research Chemicals, Inc., P.O. Box 1778, Gainsville, Fla. 32602; No. 11898-4.

of an organized collection of many thousands of compound spectra stored in a large central computer accessed by the analyst through telephone linkups. On the basis of 8 or 10 major masses the computer can rapidly search the complete system for similar spectra. These spectra are ranked for similarity to the unknown using a mathematical algorithm. The resulting similarity index (SI), which can be further refined to a quality index (2), is a measure of the degree of confidence the analyst may place in the identification. If a match is not found, the analyst must revert to manual interpretation of the spectra and deduce the structure of the compound by its fragmentation patterns.

After a tentative identification is made, several other types of supporting experiments become possible. Retention-time GC/MS data of a pure compound (standard) may be compared with analogous data from the sample component. Similarly, the mass spectrum of the standard, obtained under the same conditions that were used for the sample, may be compared with the sample component spectrum. The standard may be dissolved in water at an appropriate concentration, isolated, and measured. The recovery of this spike in the same fraction in which the suspected component appeared and the observation of equivalent mass spectra for the spike and the sample component constitute strong evidence for confirmation of the identification.

8.6 References

1. Methods for Organic Analysis of Water and Wastes, U.S. EPA, EMSL, Environmental Research Center, Cincinnati (in preparation).
2. EPA GC/MS Procedural Manual, Budde, W. L., and Eichelberger, J. W., editors, 1st Edition, Vol. 1, U.S. EPA, Office of Research and Development, EMSL, Cincinnati (in press).
3. Eichelberger, J. W., Harris, L. E., and Budde, W. L., Anal. Chem., *47*, 995 (1975).

Chapter 9

SKILLS AND TRAINING

9.1 General

Analytical operations in the laboratory can be graded according to the degree of complexity. Some analyses require no sample treatment, and the measurement can be performed in minutes on a simple instrument. Other determinations require extensive sample preparation prior to complex instrumental examination. Consequently, work assignments in the laboratory should be clearly defined. Each analyst should be completely trained and should fully understand all the assignments of his job before being given new responsibilities. In this regard, all analysts, subprofessional or professional, should be thoroughly instructed in basic laboratory operations, according to the degree of professional maturity. Some of the basic operations that should be reviewed periodically with laboratory personnel follow.

9.1.1 Sample Logging

Routine procedure for recording of samples entering the laboratory and assigning primary responsibility should be emphasized. The information that is required and the routing of the sample to the analyst is then established. The stability, preservation, and storage of samples prior to analyses are then discussed.

9.1.2 Sample Handling

The analyst should understand thoroughly at which points in his procedures the sample is to be settled, agitated, pipetted, etc., before he removes it from the original container.

9.1.3 Measuring

The analysts, especially new employees and subprofessionals, should be instructed in the use of volumetric glassware. The correct use of pipettes and graduates should be emphasized as discussed in chapter 4 of this manual.

9.1.4 Weighing

Because almost every measuring operation in the analytical laboratory is ultimately related to a weighing operation, the proper use of the analytical balance should be strongly emphasized. Maintenance of the balance, including periodic standardization, should be repeatedly emphasized to all personnel. The correct use and maintenance of balances is discussed in chapter 3 of this manual.

9.1.5 Glassware

All glassware should be washed and rinsed according to the requirements of the analysis to be performed. Not only must the personnel assigned to these tasks be instructed, but also all lab personnel should know the routine for washing and special requirements for particular uses of glassware. In addition, the precision tools of the laboratory such as pipets, burets,

graduates, and Nessler tubes should be inspected before use for cleanliness, broken delivery tips, and clarity of marking. Defective glassware should be discarded or segregated.

9.1.6 Instrumentation

Operation and maintenance of analytical instrumentation is of primary consideration in the production of valid data. All instruments must be properly calibrated, quality-control checks documented, and standard curves verified on a routine basis. Details on instrumental quality control are presented in chapter 3 of this manual.

9.1.7 Data Handling and Reporting

As with sample logging, the routine procedure for recording results of analyses and pertinent observations, including quality control checks, should be emphasized. Analytical data should be permanently recorded in meaningful, exact terms and reported in a form that permits future interpretation and unlimited use. Details are discussed in chapter 7 of this manual.

9.1.8 Quality Control

The need to continuously assess precision and recovery values of methodology is a prime responsibility of the analyst. Self-evaluation through the analyses of replicates and recovery of spikes from samples representative of the daily workload provides confidence and documentation of the quality of the reported data.

9.1.9 Safety

Laboratory safety should be discussed on a continuing basis with all employees, but it should be emphasized when an employee is assigned to perform new duties.

9.1.10 Improvement

In summary, quality control begins with basic laboratory techniques. Individual operator error and laboratory error can be minimized if approved techniques are consistently practiced. To insure the continued use of good technique, laboratory supervisors should periodically review the basic techniques and point out areas of needed improvement with each analyst.

Continuing improvement of technical competence by all laboratory personnel is, of course, the final responsibility of the laboratory supervisor. In a well-organized laboratory, however, a big-brother attitude of higher ranking to lower grade personnel should be encouraged; each person should be eager to share experience, tricks of the trade, special skills, and special knowledge with subordinates. Obviously, efficiency and results will improve.

9.2 Skills

The cost of data production in the analytical laboratory is based largely upon two factors: the pay scale of the analyst, and the number of data units produced per unit of time. However, because of the large variety of factors involved, estimates of the number of measurements that can be made per unit of time are difficult. If the analyst is pushed to

Table 9-1
SKILL-TIME RATING OF STANDARD ANALYTICAL OPERATIONS

Measurement	Skill Required (Rating No.)[1]	Number Per Day
Simple Instrumental:		
pH	1	100-125
Conductivity	1	100-125
Turbidity	1	75-100
Color	1	60-75
Dissolved Oxygen (Probe)	1,2	100-125
Fluoride (Probe)	1,2	100-125
Simple Volumetric:		
Alkalinity (Potentiometric)	1	50-75
Acidity (Potentiometric)	1	50-75
Chloride	1	100-125
Hardness	1	100-125
Dissolved Oxygen (Winkler)	1,2	75-100
Simple Gravimetric:		
Solids, Suspended	1,2	20-25
Solids, Dissolved	1,2	20-25
Solids, Total	1,2	25-30
Solids, Volatile	1,2	25-30
Simple Colorimetric:		
Nitrite N (Manual)	2	75-100
Nitrate N (Manual)	2	40-50
Sulfate (Turbidimetric)	2	70-80
Silica	2	70-80
Arsenic	2,3	20-30
Complex, Volumetric, or Colorimetric:		
BOD	2,3	[2]15-20
COD	2,3	25-30
TKN	2,3	25-30
Ammonia	2,3	25-30
Phosphorus, Total	2,3	50-60
Phenol (Distillation Included)	2,3	20-30
Oil and Grease	2,3	15-20
Fluoride (Distillation Included)	2,3	25-30
Cyanide	2,3	8-10
Special Instrumental:		
TOC	2,3	75-100
Metals (by AA), No Preliminary Treatment	2,3	150
Metals (by AA), With Preliminary Treatment	2,3	60-80
Organics (by GC), Pesticides, Without Cleanup	3,4	3-5
Organics (by GC), Pesticides, With Cleanup	3,4	2-4

[1] Skill-required rating numbers are defined as follows:
1—aide who is a semiskilled subprofessional with minimum background or training, comparable to GS-3 through GS-5. (Continued)

produce data at a rate beyond his capabilities, unreliable results may be produced. On the other hand, the analyst should be under some compulsion to produce a minimum number of measurements per unit of time, lest the cost of data production become prohibitive. In table 9-1, estimates are given for the number of determinations that an analyst should be expected to perform on a routine basis. The degree of skill required for reliable performance is also indicated.

The time limits presented in the table are based on use of approved methodology. A tacit assumption has been made that multiple analytical units are available for measurements requiring special equipment, as for cyanides, phenols, ammonia, nitrogen, and COD. For some of the simple instrumental or simple volumetric measurements, it is assumed that other operations such as filtration, dilution, or duplicate readings are required; in such cases the number of measurements performed per day may appear to be fewer than one would normally anticipate.

9.3 Training

For more experienced, higher grade personnel, formal training in special fields, possibly leading to specialization, should be almost mandatory. Such training can be fostered through local institutions and through the training courses provided by the EPA. Regional policies on after-hours, Government-supported training should be properly publicized.

Formalized training for lower grade personnel, comparable to GS-3 to GS-5, is relatively scarce. However, skills can be most efficiently improved at the bench level on a personal, informal basis by more experienced analysts working in the same area. Exposure of personnel to pertinent literature should also be a definite program policy.

(Continued)

2—aide with special training or professional with minimum training with background in general laboratory techniques and some knowledge of chemistry, comparable to GS-5 through GS-7.

3—experienced analyst capable of following complex procedures with good background in analytical techniques, professional, comparable to GS-9 through GS-12.

4—experienced analyst specialized in highly complex procedures, professional, comparable to GS-11 through GS-13.

[2] Rate depends on type of samples.

Chapter 10

WATER AND WASTEWATER SAMPLING

10.1 Introduction

The quality of data resulting from water and wastewater sampling surveys is dependent upon the following six major activities: (a) formulating the particular objectives of the water sampling program, (b) collecting representative water samples, (c) maintaining the integrity of the water samples through proper handling and preservation, (d) adhering to adequate chain-of-custody and sample identification procedures, (e) practicing quality assurance in the field, and (f) properly analyzing the pollutants in the water samples. These areas are equally important for insuring that environmental data are of the highest validity and quality.

The present section addresses aspects of quality control (QC) concerned with the collection of environmental samples and data in the field. It includes a capsule summary of the specific areas mentioned previously and a list of references (table 10-1) that provide specific guidance in these areas, rather than a collection of guidelines on sampling procedures.

10.2 Areas of Sampling

The specific areas that comprise an overall water sampling program are as follows.

10.2.1 Objectives of the Particular Sampling Program

The objectives of the sampling program affect all the other aspects of the sampling program.

Sampling program objectives are determined by the following activities: (a) planning (areawide or basin), (b) permitting, (c) compliance, (d) enforcement, (e) design, (f) process control, and (g) research and development. The types of water sampling programs to be employed, depending on suitability to program objectives, include reconnaissance surveys; point-source characterization; intensive surveys; fixed-station-network monitoring; groundwater monitoring; and special surveys involving chemical, biological, microbiological, and radiological monitoring.

Factors that must be considered in meeting the objectives of the sampling program are the extent of the manpower resources, the complexity of the parameters of interest, the duration of the survey, the number of samples, the frequency of sampling, the type of samples (grab or composite), and the method of sample collection (manual or automatic).

10.2.2 Collection of Representative Samples

The objective of all water and wastewater sampling is to obtain a representative portion of the total environment under investigation. The techniques for obtaining representative water samples may vary with the length, width, and depth of a body of water, its physical and chemical parameters, and its type to be sampled (such as municipal or industrial effluents, surface waters and bottom sediments, agricultural runoff, and sludges). In collecting representative samples, the following factors should be considered.

Table 10-1
GUIDANCE FOR WATER/WASTEWATER SAMPLING

Sampling Subject Area	Reference Numbers											
	1	2	3	4	5	6	7	8	9	10	11	12
Objectives of a Sampling Program	X					X	X					
Collection of Representative Samples:	X	X										
Site Selection	X	X					X	X				
Sample Types[1]	X	X				X	X					
Automatic Samplers	X	X		X	X	X	X					X
Flow Measurement	X	X				X	X		X	X		X
Statistical Approach to Sampling:	X											
Frequency of Sampling	X					X						
Number of Samples	X					X						
Probability of Exceeding Standard	X					X						
Special Sampling Procedures:												
Municipal Wastewaters	X											X
Industrial Wastewaters	X											
Agricultural Wastewaters	X											
Surface Waters	X											
Bottom Sediments	X											
Sludges	X											
Biology	X		X				X					
Microbiology	X					X		X				
Radiation	X	X					X	X				
Sample Preservation and Handling:	X	X				X	X	X			X	X
Volume of Sample	X	X									X	
Container Type and Cleaning	X	X										
Sample Identification	X	X						X				
Chain of Custody	X	X						X				
Quality Assurance in the Field		X										

[1] Grab, composite, manual, etc.

10.2.2.1 Site Selection

The location of the sampling site is critical in obtaining representative data. Preferably, water sampling sites for point sources of pollution from municipal and industrial effluents are located at points of highly turbulent flow to insure good mixing; however, inaccessibility, lack of site security, or power unavailability may preclude use of the best sites, but these impediments should not be used as reasons for collecting samples at unacceptable locations. Locations of sampling sites for streams, lakes, impoundments, estuaries, and coastal areas vary, but in general occur in the following bodies: (a) in water bodies for sensitive uses (swimming and drinking water supply), (b) in major impoundments or reservoirs near the mouths of major tributaries and in the rivers entering and leaving the impoundments, (c) in water bodies polluted by man's activities, (d) in rivers upstream and downstream from tributaries, and (e) where hydrological conditions change significantly.

10.2.2.2 Types

The basic types of water and wastewater sampling methods are grab sampling and composite sampling. Composite sampling may be conducted manually or automatically. The six methods for forming composite samples, all of which depend on either a continuous or periodic sampling mode, are the following: (a) constant sample pumping rates, (b) sample pumping rates proportional to stream flow rates, (c) constant sample volumes and constant time intervals between samples, (d) constant sample volumes and time intervals between samples proportional to stream flow rates, (e) constant time intervals between samples and sample volumes proportional to total stream flow volumes since last sample, and (f) constant time intervals between samples, and sample volumes proportional to total stream flow rates at time of sampling. The choice of using the grab sampling method or one of the six compositing sampling methods is determined by program objectives and the parameters to be sampled.

10.2.2.3 Automatic Samplers

The use of automatic samplers eliminates errors caused by the human element in manual sampling, reduces personnel cost, provides more frequent sampling than practical for manual sampling, and eliminates the performance of routine tasks by personnel. Criteria for brand selection of automatic samplers include evaluations of the intake device, intake pumping rates, sample transport lines, sample gathering systems (including pumps and scoops), power supplies and power controls, sample storage systems, and additional desirable features to fit particular sampling conditions. There are many commercially available automatic samplers; however, because no single automatic sampler is ideally suited for all situations, the user carefully selects the automatic sampler most suited for the particular water or wastewater to be characterized. Precautions must be taken in regard to using certain types of samples in potentially explosive atmospheres.

10.2.2.4 Flow Measurement

An essential part of any water or wastewater sampling survey as well as a necessary requirement of the National Pollution Discharge Elimination System (NPDES) permit program is accurate flow measurement, which can be divided into four categories:

a. Flow measurement in completely filled pipes under pressure—common devices employed are orifices, Venturi tubes, flow nozzles, Pitot tubes, magnetic flow meters, ultrasonic flow meters, and elbow meters.

b. Trajectory methods, either full or partially full, measured at the end of the pipe--common flow measurement methods are the California and Purdue pipe methods. These methods are normally considered as estimates rather than accurate measurements.

c. Flow measurement in open channels and sewers—common methods are the velocity-area measurement, time-of-passage measurement, and level measurement methods using weirs and flumes.

d. Miscellaneous flow measurement methods—common methods include use of Manning formula, tracer and salt dilution techniques, water meters, pump rates, and measurements of level changes in tanks and calibrated vessels.

Flow measurement data may be instantaneous or continuous. For continuous measurements, a typical system consists of primary devices such as weirs and flumes and secondary devices such as flow sensors, transmitting equipment, recorders, and totalizers. The improper installation or design of a primary device or malfunction of any part of a secondary device results in erroneous flow data. The accuracy of flow measurement data also varies widely, depending principally on the accuracy of the primary device and the particular flow measurement method used. In any case, an experienced investigator should be able to measure flow rates within ±10 percent of the true values.

10.2.2.5 Statistical Approach to Sampling

Four factors must be established for every sampling program: (a) number of samples, (b) frequency of sampling, (c) parameters to be measured, and (d) sampling locations. These factors are usually determined in varying degrees by details of the pertinent discharge permits or are more arbitrarily set by the program resource limitations. Nevertheless, the nature of the statistical methods selected and scientific judgment should be used to establish the best procedures.

10.2.2.6 Special Sampling Procedures

Special sampling procedures should be employed for municipal, industrial, and agricultural waters, surface waters as well as bottom sediments and sludges, and for biological, microbiological, and radiological studies.

10.2.3 Sample Preservation and Handling

During and after collection, if immediate analysis is not possible, the sample must be preserved to maintain its integrity. The only legally binding reference EPA has for sample preservation methods is the NPDES permit program specified in reference 13. However, these sample preservation procedures serve as a guide for other program objectives.

Proper handling of the samples helps insure valid data; consideration must also be given to care of the field container material and cap material, cleaning, structure of containers, container preparation for determination of specific parameters, container identification, and volumes of samples.

10.2.4 Chain-of-Custody Procedures

All programs involved in water and wastewater surveys should document and implement a chain of possession and custody of any sample collected, whether or not the resulting data are to be used in enforcement cases. Such procedures insure that the samples are collected, transferred, stored, analyzed, and destroyed only by authorized personnel. See section 12.7 for detailed procedures that can be used on all sample types.

10.2.5 Quality Assurance in the Field

Quality assurance programs for sampling equipment and for field measurement procedures (of such parameters as temperature, dissolved oxygen, pH, and conductance) are necessary to insure data of the highest quality. A field quality assurance program administered by a quality assurance coordinator should contain the following documented elements:

a. The analytical methodology; the special sample handling procedures; and the precision, accuracy, and detection limits of all analytical methods used.

b. The basis for selection of analytical and sampling methodology. For example, all analytical methodology for NPDES permits shall be that specified in reference 13, or shall consist of approved alternative test procedures. Where methodology does not exist, the quality assurance plan should state how the new method will be documented, justified, and approved for use.

c. The amount of analyses for quality control (QC), expressed as a percentage of overall analyses, to assess the validity of data. Generally, the complete quality assurance program should approximate 15 percent of the overall program with 10 and 5 percent assigned to laboratory QC and field QC, respectively. The plan should include a shifting of these allocations or a decrease in the allocations depending upon the degree of confidence established for collected data.

d. Procedures for the recording, processing, and reporting of data; procedures for review of data and invalidation of data based upon QC results.

e. Procedures for calibration and maintenance of field instruments and automatic samplers.

f. A performance evaluation system, administered through the quality assurance coordinator, allowing field sampling personnel to cover the following areas:

   (1) Qualifications of field personnel for a particular sampling situation.

   (2) Determination of the best representative sampling site.

   (3) Sampling technique including location of the points of sampling within the body of water, the choice of grab or composite sampling, the type of automatic sampler, special handling procedures, sample preservation, and sample identification.

   (4) Flow measurement, where applicable.

(5) Completeness of data, data recording, processing, and reporting.

(6) Calibration and maintenance of field instruments and equipment.

(7) The use of QC samples such as duplicate, split, or spiked samples to assess the validity of data.

g. Training of all personnel involved in any function affecting the data quality.

Quality assurance in sample collection should be implemented to minimize such common errors as improper sampling methodology, poor sample preservation, and lack of adequate mixing during compositing and testing. The checks listed in the following sections will help the quality assurance coordinator to determine when the sample collection system is out of control.

10.2.5.1 Duplicate Samples

At selected stations on a random time frame duplicate samples are collected from two sets of field equipment installed at the site, or duplicate grab samples are collected. This provides a check of sampling equipment and technique for precision.

10.2.5.2 Split Samples

A representative subsample from the collected sample is removed and both are analyzed for the pollutants of interest. The samples may be reanalyzed by the same laboratory or analyzed by two different laboratories for a check of the analytical procedures.

10.2.5.3 Spiked Samples

Known amounts of a particular constituent are added to an actual sample or to blanks of deionized water at concentrations at which the accuracy of the test method is satisfactory. The amount added should be coordinated with the laboratory. This method provides a proficiency check for accuracy of the analytical procedures.

10.2.5.4 Sample Preservative Blanks

Acids and chemical preservatives can become contaminated after a period of use in the field. The sampler should add the same quantity of preservative to some distilled water as normally would be added to a wastewater sample. This preservative blank is sent to the laboratory for analysis of the same parameters that are measured in the sample and values for the blank are then subtracted from the sample values. Liquid chemical preservatives should be changed every 2 weeks—or sooner, if contamination increases above predetermined levels.

10.2.5.5 Precision, Accuracy, and Control Charts

A minimum of seven sets each of comparative data for duplicates, spikes, split samples, and blanks should be collected to define acceptable estimates of precision and accuracy criteria for data validation.

10.2.5.6 Calibration of Field Equipment

Plans should be developed and implemented for calibrating all field analysis test equipment and calibration standards to include the following: (a) calibration and maintenance intervals, (b) listing of required calibration standards, (c) environmental conditions requiring calibration, and (d) a documented record system. Written calibration procedures should be documented and should include mention of the following:

a. To what tests the procedure is applicable.

b. A brief description of the calibration procedure. (A copy of the manufacturer's instructions is usually adequate.)

c. A listing of the calibration standard, the reagents, and any accessory equipment required.

d. Provisions for indicating that the field equipment is labeled and contains the calibration expiration date.

10.3 References

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Chapter 11

RADIOCHEMISTRY

11.1 Introduction

The objective of this chapter is to provide general information and suggestions that enable the analyst to execute his responsibilities in analytical quality control (QC) as they relate to radiochemical analyses. Because chemical and radiochemical responsibilities should be considered together, the following requirements could be included with the items specified in the preceding chapters as tasks for the radiochemist: verifying the validity of laboratory data, recommending methodology, interpreting the results, and examining the need for standard procedures.

Environmental radiation measurements are made daily by Federal, State, local, and private agencies. The data obtained from these measurements are used by the U.S. EPA and other agencies for such purposes as estimating doses, describing health effects, establishing standards and guides, and conducting regulatory activities. It is imperative to insure the precision and accuracy of the data, so that policy decisions concerning environmental quality are based on valid and comparable data.

A radiation QC program should be designed to encourage the development and implementation of QC procedures at all levels of sample collection, analysis, data processing, and reporting. It should enable the analyst to verify his analyses and document the validity of the data. In addition, such a program allows the determination of the precision and accuracy of environmental radiochemical analyses.

11.2 Sample Collection

Analytical results can be no more meaningful than the integrity of the samples that are analyzed. Representative samples must be collected so the data for any aliquot can be related to a well-defined pollution source. For most analyses (table 11-1) the sample should be preserved at the sampling site to maintain its integrity and to minimize activity losses from absorption on container walls. If at all possible, analyses should be performed soon after receipt of the samples at the laboratory.

Sample container types and descriptions have already been discussed. Both plastic and glass containers have been recommended, and each has its particular merit. Cost most likely determines which of the many types of plastic containers will be used; in general, those more expensive should be more resistant to adsorption losses. Because sample analyses are recommended soon after collection, less expensive plastic ware can be tolerated. In any event, containers should be discarded after use to prevent contamination of subsequent samples.

Glass bottles are popular items, readily available in all sizes. Although the possibility of breakage either in handling or shipping is obviously great, the very small sizes for radioactive tracer standards and calibration sources can withstand breakage. Use of the larger size bottles for these purposes should therefore be avoided. It is poor economics to ship radioactive samples in fragile glass containers when unbreakable types serve the purpose much better.

Table 11-1
SAMPLE HANDLING, PRESERVATION, METHODOLOGY, AND MAJOR INSTRUMENTATION REQUIRED[1]

Parameter	Sample Preservation[2]	Container[3]	Instrumentation
Gross Alpha Activity	Concentrated HNO_3 to pH < 2	P or G	Low-background proportional counter
Gross Beta Activity	Concentrated HNO_3 to pH < 2	P or G	Low-background proportional counter
Strontium-89	Concentrated HNO_3 to pH < 2	P or G	Low-background proportional counter
Strontium-90	Concentrated HNO_3 to pH < 2	P or G	Low-background proportional counter
Radium-226	Concentrated HNO_3 to pH < 2	P or G	Scintillation cell system
Radium-228	Concentrated HNO_3 to pH < 2	P or G	Low-background proportional counter
Cesium-134	Concentrated HCl to pH < 2	P or G	Low-background proportional counter
Iodine-131	None	P or G	Low-background proportional counter
Tritium	None	G	Liquid scintillation counter
Uranium	Concentrated HNO_3 to pH < 2	P or G	Fluorometer
Photon Emitters	Concentrated HNO_3 to pH < 2	P or G	Gamma spectrometer

[1] See reference 1 for method.
[2] Preservative to be added at the time of collection unless the sample is to be characterized for suspended solids activity.
[3] P = hard or soft plastic; G = hard or soft glass.

11.3 Laboratory Practices

11.3.1 Laboratory Safety

The general principles of laboratory safety are covered in chapter 14. The hazards to be avoided are listed, and the importance of good housekeeping practices is stressed. These practices reduce the potential hazard of the many chemical operations being performed. In the radiochemical laboratory they eliminate the probability of radiological cross-contamination from sample to sample and from sample to glassware. Many of the materials used in the laboratory are potentially hazardous because of their chemical properties or their radioactivity and therefore should be handled with the utmost care and respect.

In the radiochemical laboratory, the prevention of contamination by radioactive materials requires attention to radiation-protection practices, an ongoing personnel-monitoring program, and the designation of a segregated storage area for radioactive sources following use in radiochemical analyses. Adequate labeling of work areas, of samples for analysis, of aliquots, and of separated fractions helps to control radiation hazards and to insure personnel safety.

The handling of radioactive materials involves safety hazards of a type not usually associated with a chemical laboratory. Special precautions and instruments should be used to insure the greatest personal safety. It is imperative to wear monitoring devices (personal film badges) at all times.

A number of health and contamination hazards are to be considered. Many radioactive materials are dangerous even in extremely minute quantities if inhaled or ingested. All radioactive materials are capable of contaminating laboratories, instruments, and clothing. All radioactive materials in large concentrations are dangerous because of the effects of their radiation external to their containers. To control these hazards, the following rules should be in effect at all times.

a. For the case of radioactive materials that are capable of being volatilized or airborne, perform all work in a closed area or hood. Perform distillations, evaporations, and other such processes in a well-ventilated hood.

b. Do not bring food or liquid refreshments into a laboratory engaged in work with radioactive materials. The same applies to the counting rooms.

c. Do not smoke when handling radioactive materials.

d. After working with radioactive materials, wash hands thoroughly before eating or handling uncontaminated materials.

11.3.2 Laboratory Analyses

Standard radiochemical procedures or their equivalent are needed to comply with sensitivity detection limits for each nuclide as designated by the quality assurance program (2). Radiochemical procedures have been compiled for a multitude of nuclides in a multitude of media (3-9) and descriptions of specific separations are to be found in the scientific literature. As laboratory techniques become more sophisticated and as more sensitive instrumentation is developed, these procedures will be improved.

Depending on the media, the radioactivity levels, and the nuclide composition, there are several approaches that can be made when a sample is received for QC determination. The requirements for an acceptable QC program are described in section 11.4.

Before starting such a program, the laboratory should be already set up for radiochemical analyses and the analysts should have the prescribed education and experience.

11.3.3 Laboratory Radiation Instruments

The types of radiation counting systems (described in ref. 2) needed to comply with the requirements are set forth in the following paragraphs. Only those instruments needed for analyzing specific radionuclides are required. Such instruments should meet the specifications discussed in the next sections.

11.3.3.1 Liquid Scintillation System

A liquid scintillation system must measure tritium with the sensitivity required by the National Interim Primary Drinking Water Regulations. Efficiency of the system should be greater than 57 percent for tritium. The tritium figure of merit $(E_\tau)^2/B$ should be greater than 100.

11.3.3.2 Gas-Flow Proportional Counting System or Alternative

A gas-flow proportional counter, or the alternative described later, is required for measurement of gross alpha- and gross beta-particle activities, radium-228, strontium-89, cesium-134, and iodine-131. The detector may be either windowless (internal proportional counter) or of the thin-window type. A minimum shielding equivalent of 5 cm of lead must surround the detector. A cosmic (guard) detector should be operated in anticoincidence with the main detector. The main detector should have an efficiency greater than 20 percent for polonium-210 and carbon-14 and greater than 40 percent for strontium-90. The detector background should be less than 1.3 counts per minute.

The detector plateau should be less than 1.5 percent per 100 V and should be at least 100 V wide for carbon-14 and less than 2 percent per 100 V for strontium-90.

A scintillation system designed for alpha- and beta-particle counting may be substituted for the gas-flow proportional counter described. In such a system a Mylar disk coated with a phosphor (silver-activated zinc sulfide) is either placed directly on the sample (for alpha measurements) or on the face of a photomultiplier tube, enclosed within a light-tight container along with the appropriate electronics (high-voltage supply, amplifier(s), timer, and scaler). Radiation shielding, although desirable, is not required for this system.

11.3.3.3 Gamma Spectrometer System

A sodium iodide (NaI) detector connected to a multichannel analyzer is required for determination of manmade photon emitters. A 7.5- by 7.5-cm NaI crystal is satisfactory; however, a 10- by 10-cm crystal is recommended. The crystal detector must be shielded with a minimum of 10 cm of iron or equivalent.

It is recommended but not required that the distance from the center of the crystal detector to any part on the shield should not be less than 30 cm. The multichannel analyzer, in

addition to the appropriate electronics (high-voltage supply, preamplifier, and linear amplifier), must contain a memory of not less than 200 channels and at least one readout device.

11.3.3.4 Scintillation Cell System

A scintillation system must be designed to accept scintillation flasks (Lucas cells) for measurement of radium-226 by the radon-emanation method. The system consists of a light-tight enclosure for the scintillation flasks, a detector (phototube), and the appropriate electronics (high-voltage supply, amplifier, timers, and scalers). The scintillation flasks required for this measurement may either be purchased from commercial suppliers or constructed according to published specifications.

11.4 Quality Control

The following requirements are recommended for all laboratories:

a. All QC data should be available for inspection to determine validity of laboratory results.

b. Each laboratory should participate at least twice each year in EPA laboratory intercomparison studies (10).

c. Each laboratory should participate once each year in an appropriate EPA-administered performance study on unknowns. Results must be within the control limits established by EPA for each analysis.

d. Counting-instrument operating manuals and calibration protocols should be available to analysts and technicians.

e. Calibration data and maintenance records on all radiation instruments and analytical balances must be maintained in a permanent record.

f. Minimum daily QC

   (1) To verify precision of methods, a minimum of 10 percent of the samples shall be duplicates. Checks must be within ±2 standard deviations of the mean range.

   (2) If less than 20 samples per day are analyzed, a performance standard and a background sample must be measured. If 20 or more samples are analyzed per day, a performance standard and a background sample must be measured with each 20 samples. Checks must be within ±2 standard deviations of the mean range.

   (3) Quality control performance charts or performance records must be maintained.

11.5 References

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Chapter 12

MICROBIOLOGY

12.1 Background

The quality assurance program described in this chapter is a synopsis of a detailed program prescribed in parts IV and V of the EPA microbiological methods manual (1). Quality assurance is a program of integration of all intralaboratory and interlaboratory quality control (QC), methods standardization, and QC management practices into a formal, coordinated, continuing effort.

12.2 Specific Needs in Microbiology

A quality assurance program for microbiological analyses must emphasize the control of laboratory operations and analytical procedures because the tests measure living organisms that continually change in response to their environment. Further, because true values cannot be provided for the microbial parameters, microbiologists do not yet have the advantages of analytical standards, QC charts, and spiked samples available to other disciplines for measurement of accuracy. Because known values cannot be applied, it is important that careful and continuous control be exerted over sampling, personnel, analytical methodology, materials, supplies, and equipment.

12.3 Intralaboratory Quality Control

Intralaboratory QC is the orderly application *within a single laboratory* of laboratory practices necessary to eliminate or reduce systematic error and to control random error. This within-laboratory program must be practical, integrated, and time-efficient or it will be bypassed. When properly administered, such a program helps to insure high-quality data without interfering with the primary analytical functions of the laboratory. This within-laboratory program should be supplemented by participation of the laboratory in an interlaboratory quality assurance program such as that conducted by EPA.

Intralaboratory QC for microbiology should cover the following areas:

a. Laboratory operations

   (1) Sample collection and handling
   (2) Laboratory facilities
   (3) Laboratory personnel
   (4) Laboratory equipment and instrumentation
   (5) Laboratory supplies
   (6) Culture media
   (7) Analytical methodology

b. Analytical QC

   (1) Sterility checks
   (2) Positive and negative controls

(3) Duplicate analyses
(4) Single-analyst precision
(5) Comparison of results between analysts
(6) Verification of membrane filter analyses
(7) Completion of most probable number analyses,
(8) Data handling

12.4 Interlaboratory Quality Control

An interlaboratory quality assurance program is an agreed-upon system of minimal requirements necessary to maintain a quality standard among a group of laboratories. Such a program may be voluntary or compulsory for participants. It may include the following activities:

a. Selection and approval of uniform sampling methodology and analytical methodology

b. Collaborative studies to establish the precision and accuracy of selected methodology

c. Preparation of guidelines to set minimal group standards for personnel, equipment, instrumentation, facilities, and intralaboratory QC programs

d. Onsite inspection of laboratory capabilities

e. Periodic evaluation of laboratory performance on unknown samples

f. Followup on problems identified in onsite inspections and performance evaluations

As a part of its interlaboratory quality assurance program, EPA has selected microbiological methodology and standards for laboratory operations (1). EMSL-Cincinnati is currently conducting research on the development of QC samples for use in performance testing and method-validation studies.

12.5 Development of a Formal Quality Assurance Program

Unless records are kept of the QC checks and procedures, there is no proof of performance, no value in future reference, and for practical purposes, no quality assurance program in operation. To insure a viable quality assurance program, management must first recognize the need and require the development of a formal program, and then commit 15 percent of the laboratory man-years to QC activities. The laboratory manager holds meetings with supervisors and staff workers to establish levels of responsibility and functions of management, supervisor, and analyst in the quality assurance program. Laboratory personnel participate in planning and structuring the program.

Once the quality assurance program is functioning, supervisors review laboratory operations and QC with analysts on a frequent (weekly) basis. Supervisors use the results of the regular meetings with laboratory personnel to inform management of the status of the program on a regular (monthly) basis. These meetings identify problems through participation of laboratory personnel and provide the backing of management for actions required to correct problems.

12.6 Documentation of a Quality Assurance Program

A laboratory operating manual should be prepared that describes operation, maintenance, and QC of laboratory operations and analyses as practiced. The review mechanisms and the frequency of review in the quality-assurance program are included.

12.6.1 Sampling

A sample log is used to record information on samples received in the laboratory including details of sample identification and origin, the necessary chain-of-custody information, analyses performed, and final results.

12.6.2 Laboratory Operations

A QC record is maintained on media preparation, instrument calibration, purchase of supplies, QC checks on materials, supplies, equipment, instrumentation, facilities, and analyses.

12.6.3 Analytical Quality Control

A record of analytical QC checks is maintained on positive and negative controls, sterility checks, single-analyst precision, precision between analysts, and use-test results from comparison of lots of media, membrane filters, and other supplies.

12.7 Chain-of-Custody Procedures for Microbiological Samples

12.7.1 General

A regulatory agency must demonstrate the reliability of its evidence by proving the chain of possession and custody of any samples that are offered for evidence or that form the basis of analytical test results introduced into evidence in any water pollution case. It is imperative that the office and the laboratory prepare procedures to be followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed.

The primary objective of these procedures is to create an accurate written record that can be used to trace the possession of the sample from the moment of its collection through its introduction into evidence. A sample is in custody if it is in any one of the following states:

a. In actual physical possession

b. In view, after being in physical possession

c. In physical possession and locked up so that no one can tamper with it

d. In a secured area, restricted to authorized personnel

Personnel should receive copies of study plans prior to the study of a water pollution case. Prestudy briefings should then be held to apprise participants of the objectives, sample locations, and chain-of-custody procedures to be followed. After the chain-of-custody samples are collected, a debriefing is held in the field to verify the adherence to the chain-of-custody procedures and to determine whether additional samples are required.

12.7.2 Rules for Sample Collection

An agency or laboratory engaged in sample study activities should follow these rules:

a. Involve a minimum number of trained persons in sample collection and handling.

b. Establish guidelines for particular procedures to be used for each type of sample collection, preservation, and handling.

c. Handle samples as little as possible.

d. Obtain stream and effluent samples using the appropriate sampling techniques.

e. Attach sample tag or label securely (see fig. 12-1) to the sample container at the time the sample is collected. The tag should contain the following items as a minimum: the serial number of the tag, the station number and location, the date and time taken, the type of sample, the sequence number (e.g., first sample of the day–sequence No. 1), the preservative used, the analyses required, and the name of the sample collector. Tags should be completed legibly in waterproof ink.

f. Use bound field notebooks to record field measurements and other pertinent information necessary to reconstruct the sample collection processes in the event of a later enforcement proceeding. Maintain a separate set of field notebooks for each study and store them in a safe place where they can be protected and accounted for at all times. Establish a sample log sheet with a standard format to minimize field entries and include the serial number of the sheet, the date, time, survey, type of samples taken, volume of each sample, type of analyses, (unique) sample numbers, sampling location, field measurements (such as temperature, conductivity, dissolved oxygen (DO), and pH), and any other pertinent information or observation. (See fig. 12-2.) The entries should be signed by the sample collector. The responsibility for preparing and retaining field notebooks during and after a study should be assigned to a study coordinator or his designated representative.

g. The sample collector is responsible for the care and custody of the samples until the samples are properly dispatched to the receiving laboratory or given to an assigned custodian. The sample collector must insure that each container is in his physical possession or in his view at all times, or stored in a locked place where no one can tamper with it.

h. Take color slides or photographs of the sample locations and any visible water pollution. Sign and indicate time, date, and site location on the back of the photo. To prevent alteration, handle such photographs according to the established chain-of-custody procedures.

12.7.3 Transfer of Custody and Shipment

In transfer-of-custody procedures, each custodian or sampler must sign, record, and date the transfer. Most environmental regulatory agencies develop chain-of-custody procedures tailored to their needs. These procedures may vary in format and language but contain the same essential elements. Historically, sample transfer under chain of custody has been on a

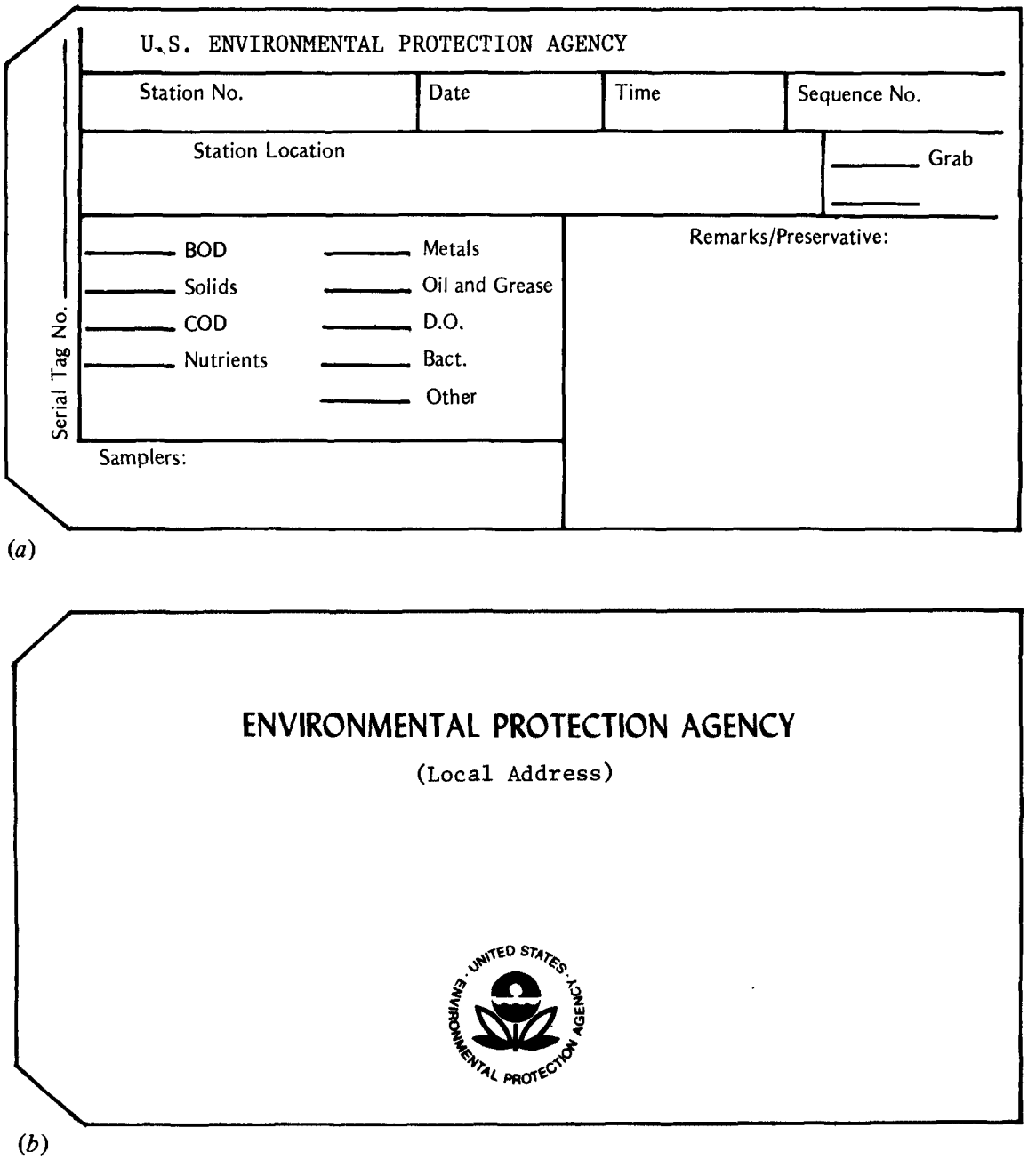

Figure 12-1. Example of chain-of-custody sample tag. (*a*) Front. (*b*) Back.

sample-by-sample basis, which is awkward and time consuming. However, the EPA National Enforcement Investigation Center (NEIC) at Denver has set precedent with its bulk transfer of samples. Bulk transfer is speedier and reduces paperwork and the number of sample custodians. The following description of bulk transfer of custody is essentially that of the Office of Enforcement (2).

FOR _____ SURVEY SAMPLE LOG SHEET NO. _____ DATE _____

TYPE OF SAMPLE _____ SAMPLER: *(Signature)* _____ ANALYSES REQUIRED

STATION NUMBER	STATION DESCRIPTION	TOTAL VOLUME	TYPE CONTAINER	PRESERVATIVE	NUTRIENTS	BOD	COD	TOC	TOTAL SOLIDS	SUSPENDED SOLIDS	ALKALINITY	DO	pH*	CONDUCTIVITY*	TEMPERATURE*	TOTAL COLIFORM	FECAL COLIFORM	TURBIDITY	OIL AND GREASE	METALS	BACTI	PESTICIDES	HERB	TRACE ORGANICS	PHENOL	CYANIDE

REMARKS

*Field Measurements

US EPA, NEIC-Denver

Figure 12-2. Example of sample log sheet.

a. Samples must be accompanied by a chain-of-custody record that includes the name of the study, collectors' signatures, station number, station location, date, time, type of sample, sequence number, number of containers, and analyses required. (See fig. 12-3.) When turning over possession of samples, the transferor and transferee sign, date, and time the record sheet. This record sheet allows transfer of custody of a

CHAIN OF CUSTODY RECORD

				SAMPLERS *(Signature)*					
STATION NUMBER	STATION LOCATION	DATE	TIME	SAMPLE TYPE			SEQ NO	NO OF CONTAINERS	ANALYSIS REQUIRED
				Water		Air			
				Comp	Grab				

Relinquished by: *(Signature)*	Received by: *(Signature)*	Date/Time
Relinquished by: *(Signature)*	Relinquished by: *(Signature)*	Date/Time
Relinquished by: *(Signature)*	Received by: *(Signature)*	Date/Time
Received by: *(Signature)*	Received by Mobile Laboratory for field analysis: *(Signature)*	Date/Time
Dispatched by: *(Signature)*	Date/Time / Received for Laboratory by:	Date/Time
Method of Shipment:		

Distribution: Orig.–Accompany Shipment
1 Copy–Survey Coordinator Field Files

Figure 12-3. Example of chain-of-custody record.

group of samples in the field to the mobile laboratory or to the central laboratory. When a custodian transfers a portion of the samples identified on the sheet to the mobile laboratory, the individual samples must be noted in the column with the signature of the person relinquishing the samples. The laboratory person receiving the samples acknowledges receipt by signing in the appropriate column.

b. If the custodian has not been assigned, the field custodian or field sampler has the responsibility of packaging and dispatching samples to the laboratory for analysis. The dispatch portion of the chain-of-custody record must be filled out, dated, and signed.

c. To avoid breakage, samples must be carefully packed in shipment containers such as ice chests. The shipping containers are padlocked for shipment to the receiving laboratory.

d. Packages must be accompanied by the chain-of-custody record showing identification of the contents. The original must accompany the shipment. A copy is retained by the survey coordinator.

e. If sent by mail, register the package with return receipt requested. If sent by common carrier, a Government bill of lading should be obtained. Receipts from post offices and bills of lading will be retained as part of the permanent chain-of-custody documentation.

f. If delivered to the laboratory when appropriate personnel are not there to receive them, the samples must be locked in a designated area within the laboratory, so that no one can tamper with them or must be placed in a secure area. The recipient must return to the laboratory, unlock the samples, and deliver custody to the appropriate custodian.

12.7.4 Laboratory Custody Procedures

Suitable laboratory procedures during custody of samples include the following:

a. The laboratory shall designate a sample custodian and an alternate custodian to act in his absence. In addition, the laboratory shall set aside a sample storage security area. This should be a clean, dry, isolated room with sufficient refrigerator space that can be securely locked from the outside.

b. Samples should be handled by the minimum possible number of persons.

c. Incoming samples shall be received only by the custodian who will indicate receipt by signing the chain-of-custody record sheet accompanying the samples and retaining the sheet as a permanent record. Couriers picking up samples at the airport or post office shall sign jointly with the laboratory custodian.

d. Immediately upon receipt, the custodian places the samples in the sample room, which will be locked at all times except when samples are removed or replaced by the custodian. To the maximum extent possible, only the custodian shall be permitted in the sample room.

e. The custodian shall insure that microbiological samples are properly stored and maintained at 4°C.

f. Only the custodian will distribute samples to personnel who are to perform tests.

g. The analyst records in his laboratory notebook or analytical worksheet, identifying information describing the sample, the procedures performed, and the results of the testing. The notes shall be dated, shall indicate who performed the tests, and should include any abnormalities that occurred during the testing procedure. The notes shall be retained as a permanent record in the laboratory. In the event that the person who performed the tests is not available as a witness at the time of a trial, the Government may be able to introduce the notes in evidence under the Federal Business Records Act.

h. Approved methods of laboratory analyses shall be used as required by Public Laws 92-500, 93-523, 92-532, and amendments.

i. Laboratory personnel are responsible for the care and custody of a sample once it is handed to them and should be prepared to testify that the sample was in their possession and view or secured in the laboratory at all times from the moment it was received from the custodian until the tests were run.

j. The laboratory area shall be maintained as a secured area and shall be restricted to authorized personnel.

k. Once the sample analyses are completed, the unused portion of the sample, together with identifying labels and other documentation, must be returned to the custodian. The returned, tagged sample should be retained in the custody room until permission to destroy the sample is received by the custodian.

l. Samples should be destroyed only upon the order of the laboratory director, in consultation with previously designated enforcement officials, or when it is certain that the information is no longer required, or that the samples have deteriorated. The same destruction procedure is true for tags and laboratory records.

12.7.5 Evidentiary Considerations

Reducing chain-of-custody procedures and promulgated analytical procedures to writing will facilitate the admission of evidence under Rule 803 (6) of the Federal Rules of Evidence (Public Law 93-575). Under this statute, written records of regularly conducted business activities may be introduced into evidence as an exception to the hearsay rule without the testimony of the person(s) who made the record. Although it would be preferable, it is not always possible for the individuals who collected, kept, and analyzed samples to testify in court. In addition, if the opposing party does not intend to contest the integrity of the sample or testing evidence, admission under Rule 803(6) can save a great deal of trial time. For these reasons, it is important that the procedures followed in the collection and analyses of evidentiary samples be standardized and described in an instruction manual, which, if need be, can be offered as evidence of the regularly conducted business activity followed by the laboratory or office in generating any given record.

In criminal cases, however, records and reports of matter observed by police officers and other law enforcement personnel are not included under the business record exceptions to the hearsay rule previously cited. (See Rule 803(8), Public Law 93-595.) It is arguable that those portions of the compliance inspection report dealing with matters other than sampling and analysis results come within this exception. For this reason, in criminal actions, records and reports of matter observed by field investigators may not be admissible, and the evidence may still have to be presented in the form of oral testimony by the person(s) who made the record or report, even though the materials come within the definition of business records. In a criminal proceeding, the opposing counsel may be able to obtain copies of reports prepared by witnesses (even if the witness does not refer to the records while testifying), which may be used for cross-examination purposes.

Admission of records is not automatic under either of these sections. The business records section authorizes admission "unless the source of information or the method or circumstances of preparation indicate lack of trustworthiness," and the caveat under the public records exception reads "unless the sources of information or other circumstances indicate lack of trustworthiness."

Thus, whether or not the inspector anticipates that a report will be introduced as evidence, the inspector should make certain that the report is as accurate and objective as possible.

12.8 References

1. Winter, J. A., Bordner, R., and Scarpino, P., Microbiological Methods for Monitoring the Environment, Part I—"Water and Wastes," U.S. EPA, EMSL, Cincinnati (1978).
2. NPDES Compliance Sampling Manual, U.S. EPA, Office of Water Enforcement (June 1977).

Chapter 13

AQUATIC BIOLOGY

Quality assurance guidelines for aquatic biology programs (fully described in ref. 1) are summarized in the following section.

13.1 Summary of General Guidelines

Successful quality assurance programs in aquatic biology are based on the following essential elements:

a. An understanding and acceptance of the importance of quality control (QC) and a commitment on the part of the biology staff to fully integrate QC practices into field and laboratory operations

b. A staff with adequate formal training and experience and proper specialization to meet program needs

c. Adequate field equipment, storage and laboratory space, instrumentation, and taxonomic references

d. Careful advance preparation and design of field and laboratory studies

e. Strict adherence to approved methodology, where available, and careful consideration of the technical defensibility of the methods and their application

f. Use of replication in sample collection and analysis where feasible, and determination of the accuracy and precision of the data

g. Frequent calibration of field and laboratory instruments

h. Proper sample identification and handling to prevent misidentification or intermixing of samples

i. Use of blind, split, or other control samples to evaluate performance

j. Development and regular use of in-house reference specimen collections, and use of outside taxonomic experts to confirm or provide identifications for problem specimens

k. Meticulous, dual-level review of the results of manual arithmetical data manipulations and transcriptions before the data are used in reports or placed in BIOSTORET (2)

l. Participation in EPA formal interlaboratory aquatic biology methods studies, and use of EPA biological reference materials

m. Documentation of methodology and QC practices employed in the program

13.2 Discussion

A brief description of each of the areas mentioned in section 13.1 is provided here to indicate the scope of the quality assurance program.

13.2.1 Staff Commitment

To establish and maintain an effective quality assurance program in aquatic biology, the supervisor must actively support and frequently monitor the use of QC practices in all aquatic biology activities. This will require the commitment of 10 to 15 percent of the total manpower resources. The supervisor must review field and laboratory operations with his staff frequently (weekly) to insure that QC practices are followed and properly documented.

13.2.2 Staff

The quality and reliability of the data rest heavily on the competence of the staff. The range of aquatic organisms studied by biological programs is very broad, and each community requires unique skills in sample collection and analysis, and in data interpretation. Several disciplines, therefore, must be represented on the staff to deal effectively with the taxonomy and ecology of the major groups of aquatic organisms, which include the phytoplankton, zooplankton, periphyton, macrophyton, macroinvertebrates, and fish.

13.2.3 Facilities

The quality of the data also depends upon the availability and performance of laboratory equipment. Such items as sampling gear, current meters, spectrophotometers, and microscopes must be available and must meet performance standards related to the biological parameters measured. Laboratory instrumentation must provide the sensitivity and accuracy required by the state of the art in sample analysis. Adequate laboratory and storage space must also be provided.

13.2.4 Advance Planning

Thorough advance planning of field and laboratory projects is necessary to maintain the required control over the technical aspects of the project and to insure the collection of meaningful data. Factors taken into consideration include the objectives of the study, the parameters to be measured, station selection, the sampling frequency and replication, seasonal cycles in the properties of communities of aquatic organisms, and QC measures to be incorporated into the various phases of the project.

13.2.5 Use of Approved Methodology

Methods in the EPA manual "Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents" (1) should be employed where applicable. The manual contains concensus methods selected by a committee of senior Agency aquatic biologists as the preferred methods for use within EPA. If program activities require methods for parameters not covered by reference 1, methods may be selected from other sources if their application is technically defensible.

13.2.6 Replication

Comparisons of biological parameters measured in control and affected regions of water bodies, and in laboratory experiments, may be meaningless if the precision of the results is not known. Preliminary measurements must be made in each study to determine the scatter in the data and to establish the number of replicate samples required to achieve the level of precision required to detect differences in the responses measured.

13.2.7 Instrument Calibration and Maintenance

Sampling equipment and laboratory instrumentation with mechanical metering devices and electronic components are calibrated on a regularly scheduled basis to insure the accuracy of the data. Standards are obtained, such as NBS-certified thermometers for temperature-measuring devices, class-S weights for balances, and absorption filters for spectrophotometers. Records of calibrations, regular performance checks, and service for each device are maintained in bound log books in such a manner that the history of performance of the instruments may be easily reviewed. Analytical reagents are labeled and dated when received, and are protected from deterioration if labile. The expected shelf life of each reagent is recorded on the label, and the material is not used after the expiration date.

13.2.8 Sample Labeling

Samples are securely labeled in the field and recorded in a bound log. Information on the label should include the station, date, time of day, depth, and other relevant information. A unique lot number is assigned to the sample and recorded on the label. Waterproof paper and ink must be used for the labels, and are recommended for the field logs. Depending on requirements, labels are placed inside samples such as macroinvertebrates.

13.2.9 Quality Control Samples

The accuracy of the data from routine analyses such as counts and identification of organisms and chlorophyll and biomass measurments is determined by introducing blind, split, or reference samples in the sample processing stream. These samples are either prepared by the supervisory aquatic biologist, laboratory quality control officer, or analytical QC coordinator, or are obtained from EMSL-Cincinnati. The results are discussed at regularly scheduled staff meetings and any problems identified are discussed and corrected.

13.2.10 Organism Identification and Reference Specimens

Accurate identification of aquatic organisms to the species level is essential to the interpretation of biological data. A set of reference specimens is established within each laboratory, to be used as taxonomic (identification) standards in processing samples and in training new personnel. The set is representative of the aquatic organisms collected by the program, and each specimen embodies the morphological characteristics essential to the identification of that taxon. The identity of these specimens is verified by outside taxonomic experts, who also examine organisms that pose unusually difficult identification problems in routine sample analysis.

13.2.11 Data Records, Editing (Proofing), Review

Data collected manually are entered in a bound log or on specialized bench sheets that fully describe the origin and nature of the sample and that are maintained in a binder or file. Source data such as organism abundance, metabolic rates, and chlorophyll, which are manually or electronically manipulated or transcribed from one record to another, are doublechecked by a second person. All manual calculations and all electronic calculations, where data are manually keyboarded, are performed twice, except where the source (input) data are included in the output and can be proofed. Keyboarded data are carefully proofed before they are submitted for computer manipulation.

13.2.12 Interlaboratory Methods Studies

The aquatic biology programs participate in formal interlaboratory biological methods studies performed by EMSL-Cincinnati. Studies on chlorophyll and macroinvertebrate identification methods have been completed, and additional studies on phytoplankton and periphyton identification methods are planned in the future.

13.2.13 Documentation for the Quality Assurance Program

A laboratory operations manual is available (1) that describes the scope of the program, organizational structure, qualifications of the staff, available space and equipment, methodology employed for sample collection and analysis, and QC procedures.

13.3 References

1. Weber, C. I., Editor, Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents, 2d Edition, EPA-670/4-73-001, U.S. EPA (July 1973).
2. Nacht, L., and Weber, C. I., BIO-STORET Final Design Specification, U.S. EPA (1976).

Chapter 14

LABORATORY SAFETY

14.1 Law and Authority for Safety and Health

Public Law 91-596 is the Occupational Safety and Health Act of 1970 (1). The purpose of this act is the following:

> To assure safe and healthful working conditions for working men and women; by authorizing enforcement of the standards developed under the act; by assisting and encouraging the States in their efforts to assure safe and healthful working conditions; by providing for research, information, education, and training in the field of occupational safety and health; and for other purposes.

The intent of the act (1) is "to assure so far as possible every working man and woman in the Nation safe and healthful working conditions and to preserve our human resources."

The responsibility for promulgating and enforcing occupational safety and health standards rests with the Department of Labor. The Department of Health, Education, and Welfare is responsible for conducting research on which new standards can be based, and for implementing education and training programs for producing an adequate supply of manpower to implement the purposes of the act. These responsibilities are performed by the National Institute for Occupational Safety and Health (NIOSH).

Section 19(a) of Public Law 91-596 states the following (1):

> It shall be the responsibility of the head of each Federal agency to establish and maintain an effective and comprehensive occupational safety and health program that is consistent with the standards promulgated under section 6. The head of each agency shall (after consultation with representatives of the employees thereof)–
>
> (1) provide safe and healthful places and conditions of employment, consistent with the standards set under section 6;
>
> (2) acquire, maintain, and require the use of safety equipment, personal protective equipment, and devices reasonably necessary to protect employees;
>
> (3) keep adequate records of all occupational accidents and illnesses for proper evaluation and necessary corrective action;
>
> (4) consult with the Secretary with regard to the adequacy as to form and content of records kept pursuant to subsection (a)(3) of this section; and
>
> (5) make an annual report to the Secretary of Labor with respect to occupational accidents and injuries and the agency's program under this section. Such report shall include any report submitted under section 7902(e)(2) of title 5, United States Code.

Executive Order 11807 was issued in the fall of 1974 to provide general direction to the heads of Federal agencies and to the Secretary of Labor in establishing occupational safety and health programs in the Federal Government. The executive order details the following duties:

a. Appointment of a Safety and Health Official.

b. Establishment of a management information system.

c. Establishment of an occupational safety and health program.

   (1) Adoption of safety and health standards as effective as the Secretary of Labor's standards.

   (2) Institution of procedures for processing reports from employees on hazardous conditions.

   (3) Institution of periodic inspection of facilities.

   (4) Provision for abatement of hazards in facilities.

d. Provision for training of agency personnel.

   (1) Training of supervisors at all levels.

   (2) Training of those responsible for conducting inspections of facilities.

   (3) Training of other employees. Attention is called to the list of OSHA training requirements.

e. Assistance of the Secretary of Labor.

   (1) Compliance with the recordkeeping and reporting requirements.

   (2) Observation of the guidelines issued in 28 CFR 1960.

   (3) Cooperation with the Secretary of Labor in the performance of his responsibilities.

f. Issuance of guidelines for a safety and health program.

g. Prescription of recordkeeping and reporting requirements.

h. Provision of consulting services to Federal agencies in adoption of standards, training agency personnel, and in other matters.

i. Upon request and subject to reimbursement, performance of such services as evaluation of safety and health conditions in the agency, recommendation on the adoption of standards, inspection of facilities for safety and health hazards, and training of agency personnel in safety and health matters.

j. Evaluation of agency programs and report of the condition to the President. This item in the executive order gives to the Secretary of Labor a degree of enforcement of safety and health rules and regulations within Federal agencies.

k. Section 4 continues the Federal Advisory Council on Occupational Safety and Health. Note that at least one-third of the members are to be labor representatives.

14.1.1 Occupational Safety and Health Administration Regulations

The Occupational Safety and Health Act of 1970 covers laboratory workplaces as well as industrial and manufacturing workplaces (1). Many large laboratories have already come under the scrutiny of the Occupational Safety and Health Administration (OSHA); small and medium-sized laboratories can expect direct involvement in the future.

The 1970 act set up NIOSH within the U.S. Department of Health, Education, and Welfare. NIOSH provides OSHA with the scientific information it needs to effectively perform its regulatory function.

The initial OSHA regulations were, and in some measure still are, a collection of many well-established standards taken from industry and from standards-making groups. The American National Standards Institute, the National Safety Council, the National Fire Protection Association, and the American Society for Testing and Materials were some of the prime sources for these OSHA standards. Certain existing State health and safety regulations that predated OSHA were used to develop the Federal OSHA regulations.

Efforts are continually underway to refine and quantify current OHSA regulations through court decisions resulting from appeals of compliance citations, through continuing reviews of standards by OSHA safety compliance officers, through the work of NIOSH, and through internal reviews.

Because of the continual publication of revisions of the regulations consisting of refinements and clarifications, as well as dissemination of newly issued regulations, laboratory operators must expend great efforts to keep strictly up to date. What was permitted yesterday may not be permitted today.

The first place to start in keeping up to date on OSHA regulations is to obtain a copy of the Federal or State regulations that apply. In States not operating their own OSHA function, copies of applicable regulations are usually available without charge from the local office of the U.S. Department of Labor. In other States, copies of their regulations are available from similar State offices and boards either free or at a nominal charge. In either case, appropriate steps must be taken to keep up to date on revisions and reissues. Usually this means getting on a mailing list for automatic receipt of this material as it is published. Because entire sections of the regulations may be reissued to incorporate only a few changes, it is usually necessary to completely study these reissues to determine the actual change that has been made.

As OSHA moves more into the complicated areas of chemical and biological laboratory workplaces, the level of the compliance inspector's knowledge must be increased accordingly.

14.1.2 Federal and State OSHA

There is no completely identical OSHA standard in force throughout the United States.

A provision of the act of 1970 permits Federal OSHA to certify individual State OSHA operations when they are satisfied that applicable State regulations and compliance enforcement methods fulfill the provisions of the Federal act (1).

While many State OSHA applications are in process, the following States and territories are certified or at least provisionally certified to permit their own OSHA operation:

Alaska
Arizona
California
Colorado
Connecticut
Hawaii
Indiana
Iowa
Kentucky
Maryland
Michigan
Minnesota
Nevada
North Carolina
Oregon
South Carolina
Tennessee
Utah
Vermont
Washington
Wyoming
Virgin Islands

All other states and territories are under Federal OSHA jurisdiction.

Even though the Federal Government supports 50 percent of the cost of State OSHA programs, these States apparently would prefer that the Federal Government take on the entire cost burden for them.

An important difference between Federal and State OSHA operations lies in their jurisdictions. While State OSHAs are responsible for State-operated workplaces, Federal OSHA can only inspect Federal workplaces. It cannot enforce compliance. There is, however, a current effort by the General Accounting Office to urge Congress to remove this restriction on Federal OSHA's effectiveness in dealing with Federal workplaces.

While Federal OSHA is not permitted to offer a consulting service, most State OSHAs can and do. Some who were unaware of this difference have called local Federal OSHA offices for advice. All they succeeded in doing was to invite an inspection. Normally, however,

inspections of facilities, be they manufacturing or laboratories, are triggered by an employee's complaint or an accident report, either as required by law or through police, fire, or hospital channels.

Reactions to OSHA operations vary widely. Many laboratories have been cited for violations and have been heavily fined. Yet Dr. David Pettit, Technical Director of Kelco's operations in San Diego, says, "We feel that OSHA standards are not unrealistic, just good laboratory practice."

14.2 EPA Policy on Laboratory Safety

EPA has issued an Occupational Safety and Health Manual (3) in which policy, responsibilities, accident reporting, inspections, standards, and training are described. The Agency has also issued a Safety Management Manual (4) that contains information on safety protection plans at EPA facilities and air, water, and road safety.

The EPA Occupational Safety and Health Manual (3) establishes policy, responsibilities, and procedures for the conduct of the EPA safety and health program.

The policy of EPA is to administer its programs in a manner that assures adequate protection of its own employees and property, and that for which it has a responsibility. *Every* manager, supervisor, and employee is responsible for identifying risks, hazards, and unsafe situations or practices and for taking steps to insure adequate safety in the activities under his supervison.

A facility safety officer designated for each unit must be responsible for assisting the officer-in-charge in developing, organizing, directing, and evaluating the safety and health program and coordinating illness and inquiry reporting and recordkeeping requirements; analyzing accidents and injuries for prevention and control; and providing technical advice in the implementation of program standards and policy.

Safety in any laboratory requires continuing attention. Use of new or different techniques, chemicals, and equipment requires careful reading, instruction, and supervision, and may require consultation with other people with special knowledge or experience.

Prevention of laboratory accidents requires positive attitudes toward safety and training, and suitable information for understanding laboratory and chemical hazards and their consequences.

Responsibility for safety within the laboratories for an organization may be considered to exist at three different levels—individual, supervisory (or instructional), and organizational (or institutional).

The division of responsibility needs to be clearly assigned and accepted, steps need to be taken to see that the responsibilities are exercised, and the assignments need to be reassessed if unexpected problems develop.

Each individual who works in a laboratory is responsible for learning the health and safety hazards of the chemicals he will be using or producing, and the hazards that may occur from

the equipment and techniques he will employ, so that he can design his setup and procedures to limit the effects of any accident. The individual should investigate any accident that occurs, and record and report the apparent causes and the preventive measures that may be needed to prevent similar accidents.

The supervisor has the responsibility for giving all the necessary directions, including the safety measures to be used, and the responsibility of seeing that employees carry out their individual responsibilities. Whoever directs the activities of others has a concurrent responsibility to prevent accidental injuries from occurring as a result of the activities.

The organization of which the laboratories are part has a fundamental responsibility to provide the facilities, equipment, and maintenance for a safe working environment and to provide an organized program to make the improvements necessary for a safe working environment. Unless the organization fulfills its responsibilities, it cannot expect its supervisors, employees, or students to fulfill their responsibilities for laboratory safety.

The Environmental Protection Agency has a designated safety and health official who is responsible for assuring that formal safety and health inspections are conducted at all EPA workplaces. He will notify the Administrator regarding uncorrected safety and health deficiencies.

14.2.1 Formal Safety Inspections

Formal safety and health inspections at workplaces where there is an increased risk of accident, injury, or illness because of the nature of the work performed, as in the case of chemical operations and material-handling or material-loading operations, must be made by a safety and health specialist. A "Safety and Health Specialist" is defined in 29 CFR 1960.2(h) as a person who meets the Civil Service standards for the position of Safety Manager/Specialist GS-018, Safety Engineer GS-803, Fire Protection Engineer GS-804, Industrial Hygienist GS-690, Fire Protection Specialist/Marshall GS-081, or Health Physicist GS-1306, or who is an employee of an equally qualified military agency or nongovernment organization.

Formal safety and health inspections need not be made by a safety and health specialist at workplaces where there is little risk involved, but should be conducted by a person having sufficient training and experience in the safety and health needs of the workplaces involved to adequately perform the duties of an inspector as set forth in Executive Order 11807. Inspectors should be accompanied on formal safety and health inspections by representatives of the officer in charge of the reporting unit being inspected and representatives of the employees of such establishments. Management and employee representatives should be familiar with and maintain OSHA standards.

To insure safe and healthful working conditions for EPA employees, safety and health inspectors are authorized to enter without delay and at reasonable times, any building, installation, facility, construction site, or other area, workplace, or environment where work is performed by employees of the Agency, to inspect and investigate during regular working hours and at other reasonable times, and within reasonable limits and in a reasonable manner, any such place of employment and all pertinent conditions, structures, machines,

apparatus, devices, equipment, and materials therein; and to question privately any employee, or any supervisory employee, or any officer in charge of a reporting unit.

14.2.2 Informal Safety Inspections

An informal safety and health inspection is performed on either a scheduled or unscheduled basis by the facility safety officer, regional safety officer, supervisory management, or members of a safety and health committee. EPA Form 1440-2, Health and Safety Inspection Checklist (fig. 14-1), shall be used by the inspector or spokesman of a safety and health committee conducting the inspection to note safety and health deficiencies identified during the inspection process.

A more detailed checklist for safety evaluation of the laboratory is given in appendix A. This inspection list contains many specific recommendations and guidelines for laboratory safety.

14.3 Laboratory Safety Practices*

14.3.1 Introduction

14.3.1.1 Safe Use, Handling, and Storage of Chemicals

Chemicals in any form can be safely stored, handled, and used if their hazardous physical and chemical properties are fully understood and the necessary precautions, including the use of proper safeguards and personal protective equipment are observed.

The management of every unit within a manufacturing establishment must give wholehearted support to a well-integrated safety policy.

14.3.1.2 General Rules for Laboratory Safety

Supervisory personnel should think "safety." Their attitude toward fire and safety standard practices is reflected in the behavior of their entire staff.

A safety program is only as strong as the worker's will to do the correct things at the right time.

The fundamental weakness of most safety programs lies in too much lip service to safety rules and not enough action in putting them into practice.

Safety practices should be practical and enforceable.

Accident prevention is based on certain common standards of education and training of personnel, and provision of safeguards against accidents.

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*This description was prepared by Paul F. Hallbach, Chemist, National Training and Operational Technology Center, U.S. EPA, Cincinnati, Ohio 45268.

HEALTH AND SAFETY INSPECTION CHECKLIST

INSPECTION CONDUCTED BY	TITLE	DATE

NAME/NUMBER OF BUILDING INSPECTED *(Use separate form for each building)*	REPORTING UNIT

PART I PHYSICAL CONDITIONS *(Check each applicable Item)*

ITEM	SAT	UNSAT	ITEM	SAT	UNSAT
1 HOUSEKEEPING AND SANITATION			18 ELECTRICAL AND ELECTRONIC EQUIPMENT		
2 NON HAZARDOUS MATERIALS STORAGE			19 WATER *(anti-syphone and cross connections)*		
3 HAZARDOUS MATERIALS STORAGE			20 ELECTRICAL *(fuses, grounding, etc.)*		
4 MATERIALS HANDLING EQUIPMENT			21 COMPRESSED GAS CYLINDERS		
5 AISLES AND WALKWAYS			22 STRUCTURAL CONDITION OF BUILDING		
6 LADDERS AND STAIRS			23 PARKING AREA		
7 FLOORS, PLATFORMS AND RAILINGS			24 MOTOR VEHICLES		
8 EGRESS			25 PORTABLE TOOLS		
9 LIGHTING			26 PROTECTIVE CLOTHING AND EQUIPMENT		
10 VENTILATION			27 HAZARDOUS WARNING SIGNS		
11 FLAMMABLE OR NOXIOUS DUST OR VAPORS			28 EMISSION OF POLLUTANTS *(air, fluid, solids)*		
12 HAZARDOUS BIOLOGICAL AGENTS			29 OCCUPATIONAL NOISE EXPOSURE		
13 FIRE DETECTION DEVICES			30 MEDICAL SERVICES INCLUDING FIRST AID		
14 FIRE ALARM SYSTEM			31 PROVISIONS FOR HANDICAPPED		
15 FIRE SUPRESSION *(Including extinguishers)*			32 OTHER		
16 MECHANICAL EQUIPMENT					
17 MACHINE GUARDS AND SAFETY DEVICES					

PART II PROCEDURES AND INSTRUCTIONS *(Check each applicable item)*

33 MATERIALS HANDLING			45 FIELD OPERATIONS OTHER		
34 MOTOR VEHICLE OPERATION			46 SAFETY COMMITTEE ACTIVITY		
35 BUILDING MAINTENANCE			47 FEDERAL SAFETY COUNCIL PARTICIPATION		
36 EQUIPMENT MAINTENANCE			48 EMPLOYMENT REPRESENTATION IN SAFETY AND HEALTH PROGRAM		
37 USE OF PROTECTIVE CLOTHING AND EQUIPMENT			49 JOB ORIENTATION		
38 HAZARD MONITORING EQUIPMENT *(carbon monoxide, radiation, etc.)*			50 JOB TRAINING, INCLUDING SAFETY AND HEALTH		
39 FACILITY SELF-PROTECTION PLAN			51 SAFETY PROMOTIONAL AND MOTIVATIONAL ACTIVITIES		
40 LABORATORY OPERATIONS					
41 BOATING OPERATIONS			52 PERIODIC PHYSICAL EXAMINATIONS		
42 DIVING OPERATIONS			53 OTHER		
43 AVIATION OPERATIONS					
44 CRAFTS AND SHOPS OPERATIONS					

REMARKS *(Continue on back if necessary)* (NOTE *Use EPA Form 1440.6 to document in detail each unhealthful or unsafe condition.*)

EPA Form 1440-2 (Rev. 5-77) PREVIOUS EDITION MAY BE USED UNTIL SUPPLY IS EXHAUSTED

Figure 14-1. Health and safety inspection checklist.

14.3.2 Laboratory Design and Equipment

14.3.2.1 Type of Construction

The construction of the laboratory should generally be fire resistant or noncombustible.

Multiple story buildings should have adequate means of exit.

Stairways should be enclosed with brick or concrete walls.

Laboratories should have adequate exit doors to permit quick, safe escape in an emergency and to protect the occupants from fires or accidents in adjoining rooms. Each room should be checked to make sure there is no chance of a person being trapped by fire, explosions, or release of dangerous gases.

Laboratory rooms in which most of the work is performed with flammable liquids or gases should be provided with explosion-venting windows.

14.3.2.2 Arrangement of Furniture and Equipment

Furniture should be arranged for maximum use of available space and should provide working conditions that are efficient and safe.

Aisles between benches should be at least 4 ft wide to provide adequate room for passage of personnel and equipment.

Desks should be isolated from benches or adequately protected.

Every laboratory should have an eyewash station and a safety shower.

14.3.2.3 Hoods and Ventilation

Adequate hood facilities should be installed where highly toxic or highly flammable materials are used.

Hoods should be ventilated separately and the exhaust should be terminated at a safe distance from the building.

Makeup air should be supplied to rooms or to hoods to replace the quantity of air exhausted through the hoods.

Hood ventilation systems are best designed to have an airflow of not less than 60 ft/min (linear) across the face of the hood with all doors open, and 150 ft/min (linear) if toxic materials are involved.

Exhaust fans should be sparkproof if exhausting flammable vapors and corrosive resistant if handling corrosive fumes.

Controls for all services should be located at the front of the hood and should be operable when the hood door is closed.

All laboratory rooms should have the air changed continuously at a rate depending on the materials being handled.

Recent California OSHA regulations require the presence of a means of visual indication of the existence of the airflow in the hood and specify the height and type of hood exhaust permitted.

14.3.2.4 Electrical Services

Electrical outlets should be placed outside of hoods to afford easy access and thus protect them from spills and corrosion by gases.

Noninterchangeable plugs should be provided for multiple electrical services.

Adequate outlets should be provided and should be of the three-pole-type to provide for adequate grounding.

Rubber or nonconductive composition shoe soles should be required (except when flammable vapors are present). Shoe soles should not be of a type that readily absorbs water or other liquids.

14.3.2.5 Storage

Laboratories should provide for adequate storage space for mechanical equipment and glassware that will be used regularly.

Flammable solvents should not be stored in glass bottles over 1 l in size. Large quantities should be stored in metal safety cans. Quantities requiring containers larger than 1 gal should be stored outside the laboratory.

Explosionproof refrigerators should be used for the storage of highly volatile and flammable solvents.

Cylinders of compressed or liquefied gases should not be stored in the laboratory.

Alphabetized storage of chemicals should be avoided to prevent the unintentional mixing of two incompatible chemicals in an accident situation.

An appropriate antidote must be readily available for every stored chemical compound for which an antidote is specified.

14.3.2.6 Housekeeping

Housekeeping plays an important role in reducing the frequency of laboratory accidents. Rooms should be kept in a neat and orderly condition. Floors, shelves, and tables should be kept free from dirt and from all apparatus and chemicals not in use.

A cluttered laboratory is a dangerous place to work. Maintenance of a clean and orderly work space is indicative of interest, personal pride, and safetymindedness.

Passageways should be kept clear to all building exits and stairways.

Metal containers should be provided for the disposal of broken glassware and should be properly labeled.

Separate approved waste disposal cans should be provided for the disposal of waste chemicals.

Flammable liquids not miscible with water and corrosive materials or compounds that are likely to give off toxic vapors should never be poured into the sink.

Laboratory operators must be sure that unguarded rotating equipment such as belt-driven vacuum pumps is provided with guards all the way around and that the guards are always in place.

Whenever heavy laboratory equipment must be moved frequently, rollers should be provided. In other cases, proper lifting equipment should be available.

14.3.2.7 Fire Protection

Laboratory personnel should be adequately trained regarding pertinent fire hazards associated with their work.

Personnel should know rules of fire prevention and methods of combating fires.

Fire extinguishers (CO_2 type) should be provided at convenient locations and personnel should be instructed in their use.

Automatic sprinkler systems are effective for the control of fires in chemical laboratories.

14.3.2.8 Alarms

An *approved* fire-alarm system should be provided.

Wherever a hazard of accidental release of toxic gases exists, a gas alarm system to warn occupants to evacuate the building should be provided.

Gas masks of oxygen or compressed-air-type should be located near exits and selected personnel trained to use them.

14.3.3 Handling Glassware

14.3.3.1 Receiving, Inspection, and Storage

Packages containing glassware should be opened and inspected for cracked or nicked pieces, pieces with flaws that may become cracked in use, and badly shaped pieces.

Glassware should be stored on well-lighted stockroom shelves designed and having a coping of sufficient height around the edges to prevent the pieces from falling off.

14.3.3.2 Laboratory Practice

Select glassware that is designed for the type of work planned.

To cut glass tubing or a rod, make a straight, clean cut with a cutter or file at the point where the piece is to be severed. Place a towel over the piece to protect the hands and fingers, then break away from the body.

Large size tubing is cut by means of a heated nichrome wire looped around the piece at the point of severance.

When it is necessary to insert a piece of glass tubing or a rod through a perforated rubber or cork stopper, select the correct bore so that the insertion can be made without excessive strain.

Use electric mantels for heating distillation apparatus, etc.

To remove glass splinters, use a whisk broom and a dustpan. Very small pieces can be picked up with a large piece of wet cotton.

14.3.4 Gases and Flammable Solvents

14.3.4.1 Gas Cylinders

Large cylinders must be securely fastened so that they cannot be dislodged or tipped in any direction.

Connections, gages, regulators, or fittings used with other cylinders must not be interchanged with oxygen cylinder fittings because of the possibility of fire or explosion from a reaction between oxygen and residual oil in the fitting.

Return empty cylinders promptly with protective caps replaced.

14.3.4.2 Flammable Solvents

Store in well-ventilated designated areas.

Flash point: the temperature at which a liquid gives off vapor sufficient to form an ignitible mixture with the air near the surface of the liquid or within the vessel used.

Ignition temperature: the minimum temperature required to initiate or cause self-sustained combustion independently of the heating or heated element.

Explosive or flammable limits: for most flammable liquids, gases, and solids there is a minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. There is also a maximum proportion of vapor or gas in air above which propagation of flame does not occur. These limit mixtures of vapor or gas with air, which if ignited will just propagate flame, are known as the "lower and higher explosive or flammable limits."

Explosive range: the difference between the lower and higher explosive or flammable limits, expressed in terms of percentage of vapor or gas in air by volume.

Vapor density: the relative density of the vapor as compared with air.

Underwriter's Laboratories classification: a standard classification for grading the relative hazard of the various flammable liquids. This classification is based on the following scale:

Ether class	100
Gasoline class	90 to 100
Alcohol (ethyl) class	60 to 70
Kerosene class	30 to 40
Paraffin oil class	10 to 20

Extinguishing agents that are appropriate for each of the four classes of fires are required.

14.3.5 Chemical Hazards

14.3.5.1 Acids and Alkalies

Some of the most hazardous chemicals are the strong or mineral acids such as hydrochloric, hydrofluoric, sulfuric, and nitric.

Organic acids are less hazardous because of their comparatively low ionization potentials; however, such acids as phenol (carbolic acid), hydrocyanic, and oxalic are extremely hazardous because of their toxic properties.

Classification of acids is according to mineral or organic composition. Acids should be stored together, except that perchloric acid should not be placed next to glacial acetic acid. Picric acid should be stored separately.

14.3.5.2 Oxidizing Materials

Oxidizing agents, in contact with organic matter, can cause explosions and fire. They are exothermic and decompose rapidly, liberating oxygen, which reacts with organic compounds.

Typical hazardous oxidizing agents are–

Chlorine dioxide
Sodium chlorate; chlorates
Potassium chromate
Chromium trioxide
Perchloric acid; perchlorates

14.3.5.3 Explosive Power

Many chemicals are explosive or form compounds that are explosive and should be treated accordingly.

A few of the more common examples of this class of hazardous materials are–

Acetylides
Silver fulminate

Peroxides
Peracetic acid
Nitroglycerine
Picric acid
Chlorine and ethylene
Sodium metal
Calcium carbide

14.3.5.4 Toxicity

Laboratory chemicals improperly stored or handled can cause injury to personnel by virtue of their toxicity.

There are four types of exposure to chemicals:

a. Contact with the skin and eyes

b. Inhalation

c. Swallowing

d. Injection

Special classes of toxic agents:

a. Carcinogens—laboratory operators should recheck the OSHA 1974 regulations on carcinogens.

b. Mercury—complete cleaning of spills is essential for compliance with OSHA limits.

14.3.6 Precautionary Measures

14.3.6.1 Clothing and Personal Protective Equipment

Chemical laboratories should have special protective clothing and equipment readily available for emergency use and for secondary protection of personnel working with hazardous materials.

Equipment should be provided for adequate—

a. Eye protection

b. Body protection

c. Respiratory protection

d. Foot protection

e. Hand protection

14.3.6.2 Bodily Injury

Burns, eye injuries, and poisoning are the injuries with which laboratory people must be most concerned.

First emphasis in the laboratory should be on preventing accidents. This means observing all recognized safe practices using necessary personal protective equipment and exercising proper control over poisonous substances at the source of exposure.

So that a physician can be summoned promptly, every laboratory should post the names, telephone numbers, and addresses of doctors to be called in an emergency requiring medical care.

A consulting physician should specify the type and extent of first aid materials required for the laboratory.

14.4 Report of Unsafe or Unhealthful Condition

In EPA a procedure has been established for reporting an unsafe or unhealthful condition by the employee or supervisor. The procedure also provides for communication between the employees; supervisors; safety official; head of the unit; and, in the case of an unresolved report, the Department of Labor.

A sample of an unsafe or unhealthful condition reporting form is shown in figure 14-2, and a sample notice of an unhealthful or unsafe condition is shown in figure 14-3.

14.5 References

1. Public Law 91-596, Occupational Safety and Health Act of 1970 (Dec. 29, 1970).
2. Occupational Safety and Health Manual, U.S. EPA (Jan. 8, 1976).
3. Safety Management Manual, U.S. EPA, TN 1440.1 (Dec. 4, 1972).

RNN1440.011

REPORT OF UNHEALTHFUL OR UNSAFE CONDITION

TO:	FROM
BRIEF DESCRIPTION OF UNHEALTHFUL OR UNSAFE CONDITION	
OCCUPATIONAL SAFETY AND HEALTH STANDARD VIOLATED *(If known)*	LOCATION *(Include organization, Facility and Building)*
ACTION TAKEN BY SUPERVISOR	

SIGNATURE	EMPLOYING ORGANIZATION	DATE

EPA Form 1440-6 (Rev. 8-77) PREVIOUS EDITION MAY BE USED UNTIL SUPPLY IS EXHAUSTED. NOTE: A COPY OF THIS FORM MUST BE RETAINED BY THE ORGINATOR

Figure 14-2. Report of unhealthful or unsafe condition.

NOTICE OF UNHEALTHFUL OR UNSAFE WORKING CONDITION

TO *(Name of Officer-in-Charge of Reporting Unit)*	FROM *(Name of Inspector)*
REPORTING UNIT	Occupational Health and Safety Office Washington, D.C 20460

An inspection conducted by me on_____ at _____ revealed the following violation(s) of EPA Occupational Health and Safety Standards. These Standards have been adopted in compliance with the Occupational Safety and the Health Act of 1970, PL 91-956, Section 19.

ITEM NO.	STANDARD, REGULATION OR SECTION VIOLATED	DESCRIPTION OF VIOLATION	LOCATION OF VIOLATION	NO. OF WORKING DAYS BY WHICH VIOLATION MUST BE CORRECTED AND DATE

Subpart D of 29CFR 1960.33, Safety and Health Provisions for Federal Employees, requires that a copy of this Notice shall be posted *immediately* in a prominent place at or near each place that the violation(s) referred to in the Notice occurred. The Notice must remained posted until all violations cited therein are corrected, or for three (3) working* days, whichever period is longer. A copy of this Notice shall be sent to the Health and Safety Committee of the establishment or Reporting Unit and to any person(s) who made a report of the unhealthful or unsafe condition which precipitated this inspection pursuant to the provisions of 29CFR 1960.31.

Subpart D of 29CFR 1960.34 requires the Officer-in-Charge of the Reporting Unit to *immediately* submit an abatement plan to the Designated Agency Safety and Health Official, if, in his judgment, the correction of the violation will not be possible within thirty (30) working days*. Such plan shall contain an explanation of the circumstances of the delay in abatement; a proposed timetable for the abatement, and a summary of steps being taken in the interim to protect employees. A copy of the plan shall be sent to the Health and Safety Committee of the establishment or Reporting Unit and to any person(s) who made a report of the unhealthful or unsafe condition which precipitated this inspection pursuant to the provisions of 29CFR 1960.31.

*Under the Occupational Safety and Health Act, the term "Working Day" means Monday through Friday but does not include Saturday, Sunday, or Federal Holidays.

SIGNATURE OF HEALTH AND SAFETY OFFICER	DATE

EPA Hq Form 1440 8 (8 77)

Figure 14-3. Notice of unhealthful or unsafe condition.

APPENDIX A

SUGGESTED CHECKLIST FOR THE SAFETY EVALUATION OF EPA LABORATORY AREAS

Organization: _____ Date: _____

Location: _____ Building: _____

Room(s): _____ By: _____

Item Inspected	Yes	No	N.A.	Comments
Fire Prevention				
1. Is fire alarm facility available? [.36(b)(7)]				
2. Are all exits maintained to provide free and unobstructed egress from all parts of building? [.36(b)(4)]				
3. Are all exits free of locks or fastening devices that could prevent free escape? [.36(b)(4)]				
4. a. Is the fire detection system in working order? b. Is the sprinkler system in working order? c. Are fire doors in working order? [.36(d)(2)]				
5. Are corridors and hallways at least 44 in wide? [.37(h)(1)]				
6. Do all exits discharge directly to a street, yard, court, or other open space? [.37(h)(1)]				
7. Are all exits marked by proper sign and illuminated? Are letters in sign not less than 6 in high, 3/4 in wide? [.37(q)(8)]				
8. Is access to exits marked in all cases where the exit or the way to reach it is not immediately visible? [.37(q)(5)]				
9. Is care taken to insure that no exit signs are obscured by decorations, furniture, or equipment? [.37(q)(3)]				
10. Is exit access arranged so that it is not necessary to travel toward any high hazard area to escape? [.37(f)(5)]				

Note: Adapted from a safety inspection work sheet developed by the Center for Disease Control (CDC). The pertinent section of the Code of Federal Regulations, title 29, part 1910 is given within brackets at the end of each item.

Listed below are explanations given by OSHA to questions that are not immediately clear on the safety checklist for laboratory areas. Each explanation is numbered according to the corresponding question on the facing page.

1. Self-explanatory.

2. Self-explanatory.

3. At no time should an exit door be locked or fastened in a manner that prevents it from being *immediately* opened from the inside of the building in the event of emergency. Safety inspectors should check all doors marked "EXIT" to insure that they can be readily opened.

4a,b. The building manager should conduct periodic tests (as recommended by the manufacturer or as required by local code) to insure proper working order of the fire detection system and the automatic sprinkler system.

4c. Fire doors are designed to be closed in the event of fire. Automatic fire doors normally remain open; however, the heat produced by a fire will cause them to close. Regular fire doors are designed to stay closed at all times, except for the passage of personnel. *No fire door should ever be blocked open as this will interfere with its function.* Fire doors are typically used to enclose stairways and to separate buildings and corridors.

5. Self-explanatory.

6. An exit should never discharge into a location that could potentially trap personnel. For example, an exit should not discharge into a closed courtyard.

7. Self-explanatory.

8. A sign reading "EXIT" or similar designation, with an arrow indicating the direction, shall be placed in every location where the direction of travel to reach the nearest exit is not immediately apparent.

9. Self-explanatory.

10. In designing and maintaining exit routes from a building, care should be taken to avoid routing people through or near a high hazard area. An example of a high hazard area is a corridor or room where flammable liquids are stored.

Item Inspected	Yes	No	N.A.	Comments
11. Are aisles maintained clear and unobstructed for movement of personnel and fire-fighting equipment? [.22(b)(1)]				
12. Is all fire protection equipment and apparatus identified with the color red? [.144(a)(1)]				
13. Are portable fire extinguishers maintained fully charged and operable and kept in designated places at all times? [.157(a)(1)]				
14. Are fire extinguishers conspicuously located, readily accessible, and available along normal paths of travel? [.157(a)(2)]				
15. Are extinguishers and locations conspicuously marked to indicate intended usage? [.157(a)(4)]				
16. Are extinguishers mounted so that the top is not more than 5 ft above floor; not more than 3½ ft if weight equals more than 40 lb? [.157(a)(6)]				
17. Are all extinguishers mounted in cabinets placed so that the instructions face outward? [.157(a)(7)]				
18. Are extinguishers available suited to the class of fire anticipated in each area? [.157(b)(1)]				
19. Are extinguishers placed according to distances for proper coverage? Within 75 ft—class A. Within 50 in—class B. [.157(c)]				
20. Are extinguishers inspected, maintained, and replaced by spares when they are discharged or missing? [.157(d)]				
21. Are laboratory rooms with potential fire hazards equipped with proper extinguishers for emergency situations? [.157(b)]				
22. If flammable liquids are used in a laboratory, is the mechanical ventilation sufficient to remove vapors before they reach a hazardous concentration? [.106(e)(2)(iii)]				

11. Self-explanatory.

12. Self-explanatory.

13. Self-explanatory. During a safety inspection *all* fire extinguishers should be checked aginst the requirements of this question.

14. Fire extinguishers should *never* be located in places where they are concealed from general view.

15. Fire extinguishers must be clearly labeled to indicate the type of fire they are capable of fighting. The following code is used to classify types of fires:

    Class A—fires in ordinary combustible materials such as wood, cloth, paper, and rubber
    Class B—fires in flammable liquids, gases, and greases
    Class C—fires that involve energized electrical equipment where the electrical nonconductivity of the extinguishing medium is of importance; when electrical equipment is deenergized, extinguishers for class A or B fires may be safely used
    Class D—fires in combustible metals such as magnesium, titanium, zirconium, sodium, and potassium

16. Inspector should make certain that no fire extinguishers (other than wheeled-type extinguishers) are placed on the floor.

17. Self-explanatory.

18. See explanation to question No. 15 for classification of fire hazards. Fire extinguishers (of more than one type, if necessary) should be selected and located according to anticipated fire hazards.

19. Self-explanatory.

20. Self-explanatory.

21. In certain instances, laboratories can be fire traps. When this is the case, fire extinguishers should be provided *inside* the laboratory so that occupants can fight their way out of a fire emergency. Safety inspectors should check for escape routes to the nearest corridor when considering this question.

22. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
23. Are hose outlets within easy reach of persons standing on floor and not over 6 ft from floor? [.158(b)(1)(i)]				
24. Do all connections on dry standpipes have a sign reading "DRY STANDPIPE–FOR FIRE DEPARTMENT USE ONLY"? [.158(b)(7)]				
25. Are automatic sprinkler systems provided with at least one fire department connection with at least 4-in pipe size? [.159(b)(1)]				
26. Are fire department connections designated "AUTO SPKR" or "OPEN SPKR"? [.159(b)(4)(v)]				
27. Is there a water flow detection device on the sprinkler system that will activate the fire alarm? [.159(c)(1)]				
28. Are fire alarm boxes readily accessible and within normal path distance of 200 ft? [.163(b)(3)]				
29. Are all fire alarm systems inspected and tested at weekly intervals? [.163(c)]				
30. Are "NO SMOKING" signs posted in prohibited areas? [.106(d)(7)(iii)]				
Flammable Liquid Storage				
31. Are drums which contain flammable liquids constructed of noncombustible materials? [.106(b)(1)(i)]				
32. Are storage drums vented? [.106(b)(2)(iv)]				
33. Are flammable liquids stored in proper containers? [.106(d)(2)(i)]				
34. Are safety cans and portable containers of flammable liquids painted red with yellow band or name of contents? [.144(a)(1)(ii)]				
35. Are storage cabinets being used for storing flammable liquids? [.106(d)(3)]				
36. Are storage cabinets labeled "FLAMMABLE–KEEP FIRE AWAY"? [.106(d)(3)(ii)]				

23. This question applies to buildings equipped with water and hose standpipe systems. Hose outlets are normally located in stairways or in the corridor immediately outside the stairway.

24. Self-explanatory. The building manager should be able to answer this question.

25. Fire department connections to automatic sprinkler systems are normally located on the outside of the building being protected. The size of the connection is usually embossed on a metal plate or on the connection itself.

26. The designations "AUTO-SPKR" or "OPEN-SPKR" are found embossed on a plate at the fire department connection. Failure to display one of the designations is a violation of OSHA.

27. This question is self-explanatory. The building manager should know if the facility is equipped with a sprinkler waterflow detection device.

28. Self-explanatory.

29. This procedure should be part of a regular maintenance program.

30. The laboratory supervisor shall designate areas where smoking is prohibited and "NO SMOKING" signs shall be placed in these areas.

31. Flammable liquid storage drums should be constructed of steel or some other noncombustible material.

32. Self-explanatory.

33. Flammable liquids may be safely stored in glass containers if the total capacity of the container is 1 gal or less. Larger quantities of flammable liquids should be stored in safety cans approved by a recognized testing laboratory.

34. Self-explanatory.

35. Self-explanatory.

36. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
37. Is the storage area provided with either a gravity or mechanical exhaust ventilation system? [.106(d)(4)(iv)]				
38. Are extinguishers available where flammable or combustible liquids are stored? [.106(d)(7)]				
39. Is at least one portable fire extinguisher of rating not less than 12-B units located outside of, but not more than 10 ft from, door opening into room used for storage? [.106(d)(7)(i)(a)]				
40. Is at least one portable fire extinguisher with rating not less than 12-B units located not less than 10 ft nor more than 25 ft from flammable liquid storage located outside of a storage room but inside of a building? [.106(d)(7)(i)(b)]				
41. Are "NO SMOKING" signs posted in the flammable or combustible liquid storage areas? [.106(d)(7)(iii)]				
Electrical Hazards				
42. Are all new electrical installations and all replacements, modifications, or repairs made and being maintained in accordance with the National Electrical Code? [.309]				
43. Does the interior wiring system have a grounded conductor? i.e., three-wire system? [.309–NEC(200-2)]				
44. Do all electrical appliances have Underwriter's Laboratories Inc. approval, or that of some other nationally recognized testing laboratory? [.309–NEC(90-8)]				
45. Are the cords of all electrical equipment in good condition, not frayed or spliced, etc.? [.309–NEC(400-5)]				
46. Are cords used properly (not run under rugs)? [.309–NEC(400-4)]				
47. Is there only one plug-in per socket outlet; i.e., no multiple plug-ins to one socket? [.309–NEC(240-2)]				
48. Are the lighting levels such that good illumination is provided in all walking, working, and service areas to insure safety? [.309–NEC(110-16(e))]				

37. The building manager or engineering department should know the answer to this question.

•

38. Self-explanatory. Fire extinguishers approved for fighting class B fires should be available in flammable liquids storage areas.

39. This question is self-explanatory but should be reread several times for full comprehension. Fire extinguisher ratings are often stamped on the title plate along with other specifications. *Note:* This question is to be used *only* when inspecting flammable-liquid storage rooms.

40. This question is self-explanatory, but should be reread several times for full comprehension. *Note:* This question is to be used only when inspecting flammable liquid storage *outside* of a special designated room, but inside of a building.

41. Self-explanatory.

42. Prior to adding any new electrical facilities to a laboratory, it is the responsibility of the laboratory supervisor or building manager to check with the electrical contractor to insure that the National Electrical Code is observed. This rule is retroactive to Mar. 15, 1972.

43. All convenience outlets shall be of the three-pronged type. These outlets should be checked with a grounding tester to insure proper wiring.

44. Approved appliances will bear the label of a recognized testing laboratory.

45. Self-explanatory.

46. Self-explanatory.

47. Multiple outlet (cube) adaptors or extension cords with multiple outlet ends should not be used to plug more than one appliance into a single socket.

48. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
49. Are circuit breaker panels and cutoff switches located so as to be readily accessible? [.309–NEC(240-25(b)) and (1926.400(e))]				
50. Are all circuit breaker switches marked or labeled? [.309–NEC(240-25(e))]				
Aisles, Exits, Floors, and Stairways				
51. Are all floors kept clean and dry? [.22(a)(2)]				
52. Are all floors, areas, and passageways free from protruding nails, splinters, holes, and loose boards? [.22(a)(3)]				
53. Are aisles and passageways clear of all obstructions and in good repair? [.22(b)(1)]				
54. Are aisles and passageways wide enough to operate equipment safely? [.22(b)(1)]				
55. Is floor loading within *posted* maximum limits? [.22(d)]				
56. Does every floor opening having standard guarded railings? [.23(a)(1)]				
57. Do fixed stairs make an angle to the horizontal between 30° to 50°? [.24(e)]				
58. Are all opensided floors, platforms, ramps, 4 ft above adjacent floor or ground, guarded with railing? [.23(c)(1)]				

49. Circuit breaker cabinets should *never* be locked.

50. Each circuit breaker switch shall be labeled as to the lights, outlets, or appliances it controls.

51. Self-explanatory.

52. Self-explanatory.

53. Self-explanatory.

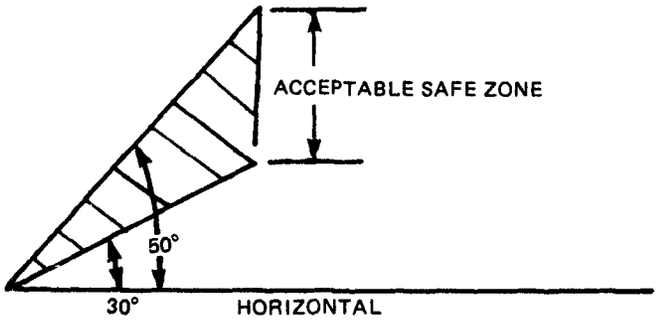
54. Self-explanatory.

55. Safe floor loadings must be *posted* and *observed* in all buildings and on all floors.

56. *Specifications for standard railing:* A standard railing shall consist of a top rail, intermediate rail, and posts. It shall have a vertical height of 42 in nominal from upper surface top rail to floor, platform, runway, or ramp level. The top rail shall be smooth surfaced throughout its length. The intermediate rail shall be approximately halfway between the top rail and the floor, platform, runway, or ramp.

    Specifications for standard railing to be used on stairways: A stair railing shall be of construction similar to a standard railing (for a floor opening), but the vertical height shall not be more than 34 in nor less than 30 in from upper surface of top rail to surface of tread in line with face of visor at forward edge of tread.

57. All fixed stairways must rise at an angle within the limits shown:



58. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
59. Are flights of stairs having four or more risers equipped with railings or handrails? [.23(d)(1)]				
60. Are stair treads reasonably uniform and slip resistant? [.24(f)]				
61. Are all places kept clean and orderly and in a sanitary condition? [.141(a)(1)(i)]				
62. Are trash receptacles of approved use? [.141(a)(3)]				
63. Is every enclosed work place so constructed and maintained to prevent entrance and harborage of rodents, insects, and vermin? [.141(a)(4)]				
64. Is drinking water potable and available within 200 ft of location at which employees work? [.141(b)(1)(i)]				
65. Are toilet facilities adequate for both sexes and in accordance with regulations listed? [.141(c)(1)]				
66. Are toilet rooms constructed so that each water closet occupies a separate compartment equipped with door, latch, and clothes hanger? [.141(c)(2)(i)]				
67. Does door to toilet room have a self-closing device, and is entrance screened so interior is not visible from outside? [.141(e)(2)(iii)]				
68. Does every water closet have a hinged open-front seat made of nonabsorbent material? [.141(c)(3)(ii)]				
69. Are suitable washing facilities available and maintained in a sanitary condition? [.141(d)(1)]				
70. If employees are allowed to lunch on the premises, is an adequate space provided for that purpose? [.141(g)(2)]				
71. Are adequate waste disposal containers provided? [.141(g)(2)]				
72. Are change rooms provided for each sex where it is necessary to change clothes? [.141(e)(1)]				
73. Are change rooms provided with separate storage facilities for street clothes and protective clothing? [.141(e)]				
74. Are noise levels acceptable? [.95]				

59. Self-explanatory.

60. Stair treads should be free of cracks and other uneven areas.

61. Self-explanatory.

62. Trash receptacles used for garbage disposal should be equipped with tight-fitting lids.

63. Self-explanatory.

64. Self-explanatory.

65. Self-explanatory.

66. Self-explanatory.

67. Self-explanatory.

68. Self-explanatory.

69. Suitable washing facilities consist of a lavatory with hot and cold water, a suitable cleansing agent, and individual hand towels.

70. Self-explanatory. Employees are *not* permitted to eat in *any* laboratory that uses agents that are dangerous to health if ingested. It is the responsibility of the laboratory supervisor to enforce this rule.

71. Self-explanatory.

72. Self-explanatory.

73. Self-explanatory.

74. If any employees are exposed to noise levels greater than 90 dB at any time during the day, a safety expert should be consulted to determine if corrective measures need to be taken.

Item Inspected	Yes	No	N.A.	Comments
75. Is necessary protective equipment provided, used, and maintained in a sanitary, safe, and reliable condition? [.132(a)]				
76. Are eye protectors provided where machines or operations present the hazard of flying objects, glare, liquids, radiation? [.133(a)]				
77. Are sufficient washing facilities (including eye washes and deluge showers) available for all persons required to handle liquids that may burn, irritate, etc.? [.151(c)]				
78. Are employees in the area exposed to air contaminants only in accordance with proper limits? [.134(a)(1)]				
79. Is a respiratory protection program used where needed? [.134(a)(2)]				
80. Are written standard operating procedures governing the selection and use of respirators established? [.134(b)(1)]				
81. Has the user of the respirator been instructed and trained in the proper use and limitations of the respirator? [.134(b)(3)]				
82. Are respirators regularly cleaned, disinfected, inspected, and stored in a convenient, clean, and sanitary location? [.134(b)(5)]				
83. Has the person assigned the task requiring a respirator been determined physically able to perform the work and use the equipment by the local physician? [.134(b)(10)]				
84. Are breathing gas containers marked in accordance with the American National Standards identifying contents? [.134(d)(4)]				
85. Can gas mask canisters be identified by properly worded labels and color code or atmospheric contaminant? [.134(g)(1)]				
86. Is the compressor for supplying air to respirators equipped with necessary safety and standby equipment? [.134(d)(2)(ii)]				

75. Protective equipment, including personal protective equipment, shall be provided, used, and maintained in a sanitary and reliable condition wherever work-associated hazards may cause injury or impairment in function of any part of the body through absorption, inhalation, or physical contact. Laboratory supervisors should recognize such hazards and take the action necessary to insure that employees use adequate personal protection to avoid injury.

76. Safety glasses or goggles may be obtained through the CDC Safety Office.

77. All laboratories using liquids that may burn or irritate must be equipped with some type of emergency eye wash equipment.

78. If laboratory supervisors have any questions concerning safety concentrations of air contaminants, they should contact the CDC Office of Biosafety.

79. Respirators that are applicable and suitable for the purpose intended shall be provided when such equipment is necessary to protect the health of employees. The CDC Office of Biosafety will provide the proper respirators for a given hazard.

80. Self-explanatory.

81. Self-explanatory.

82. Self-explanatory. Respirators should be cleaned and disinfected after each use.

83. Self-explanatory.

84. Self-explanatory.

85. Self-explanatory.

86. Compressors for breathing air should be equipped with receivers of sufficient capacity to enable the respirator wearer to escape from a contaminated atmosphere in the event of compressor failure; alarms to indicate compressor failure and overheating shall be installed in the system.

Item Inspected	Yes	No	N.A.	Comments
87. Is each employee who works in an area where radioactive material is used furnished and wearing film badge? [.96(d)(2)]				
88. Is radiation exposure of individuals to the body limited to 1¼ rems per calendar quarter? [.96(b)]				
89. Is each radiation area posted with the proper radiation caution sign? [.96(e)(2)]				
90. Are all radiation area employees instructed in the safety problems, precautions, and devices to minimize exposure? [.96(i)]				
91. Are records maintained of the radiation exposure of all employees who are monitored? [.96(n)]				
92. Are radioactive materials stored and disposed properly? Are storage containers labeled? [.96(j,k)]				
Compressed Gases				
93. Is each portable gas container for gases such as hydrogen legibly marked with the name of contents? [.252(a)(2)(i)(a)]				
94. Are compressed gas cylinders determined in safe condition by visual and other inspection required in regulations? [.101(a)]				
95. Does the compressed gas cylinder or tank have an installed pressure relief device? [.101(c)]				
96. Are all compressed gas cylinders stored and secured so they cannot fall? [.252(a)(2)(ii)(b)]				
97. Are protection caps in place on compressed gas cylinders except when in use? [.252(a)(2)(ii)(d)]				
98. Is each mobile hydrogen supply unit secured to prevent movement? [.103(b)(1)(iv)(e)]				
99. Is the hydrogen storage area permanently marked "HYDROGEN–FLAMMABLE GAS–NO SMOKING OR OPEN FLAMES"? [.103(b)(1)(v)]				

87. Self-explanatory.

88. Self-explanatory.

89. Self-explanatory.

90. Self-explanatory.

91. Self-explanatory.

92. Self-explanatory.

93. Self-explanatory.

94. Deep dents or heavy corrosion of a gas cylinder might indicate a dangerous situation.

95. Self-explanatory.

96. When either storing or moving a compressed gas cylinder, care must be taken to prevent the cylinder from falling. OSHA requires that compressed gas cylinders either be chained or strapped in an upright position at all times.

97. Self-explanatory.

Preface to Questions 98 through 107

A gaseous hydrogen system is one in which the hydrogen is delivered, stored, and discharged in the gaseous form to the consumer's piping. The system includes stationary or movable containers, pressure regulators, safety relief devices, manifolds, interconnecting piping, and controls. The system terminates at the point where hydrogen at service pressure first enters the consumer's distribution piping. Systems having a total hydrogen content of less than 400 ft^3 are *not* covered by the following questions.

98. Mobile supply units should be strapped or chained to prohibit movement.

99. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
100. Is the hydrogen system in an adequately ventilated area? [.103(b)(2)(ii)(d)(1)]				
101. Is the hydrogen system 20 ft from stored flammable materials or oxidizing gases? [.103(b)(2)(ii)(d)(2)]				
102. Is it 25 ft from open flames, electrical equipment, or other sources of ignition? [.103(b)(2)(ii)(d)(3)]				
103. Is it 25 ft from concentrations of people? [.103(b)(2)(ii)(d)(4)]				
104. Is it 50 ft from intakes of ventilation or air-conditioning equipment and air compressors? [.103(b)(2)(ii)(d)(5)]				
105. Is it 50 ft from other flammable gas storage? [.103(b)(2)(ii)(d)(6)]				
106. Is it protected from damage due to falling objects or working activity in the area? [.103(b)(2)(ii)(d)(7)]				
107. Are safety relief devices arranged to discharge upward and unobstructed to the open air and prevent impingement of gas upon container, adjacent structure, or personnel? [.109(b)(1)(ii)(b)]				
Storage				
108. Is storage of material stable and secure against sliding, collapse, falls, or spills? [.176(b)]				
109. Are storage areas kept free from accumulation of materials that constitute hazards from tripping, fire, explosion, or pest harborage? [.176(e)]				
110. Are dangerous parts of machines or energized equipment, which may injure, colored orange where exposed? [.144(a)(2)]				
111. Is yellow the color used for designating physical hazards and caution in the particular environment? [.144(a)(3)]				
112. Is the color green used to designate "SAFETY" and location of first aid equipment? [.144(a)(4)]				
113. Is purple the color used to designate radiation hazards? [.144(a)(6)]				
114. Are the colors black and white used for traffic and housekeeping markings? [.144(a)(7)]				

100. Self-explanatory.

101. Self-explanatory.

102. Self-explanatory.

103. Self-explanatory.

104. Self-explanatory.

105. Self-explanatory.

106. Self-explanatory.

107. Self-explanatory.

108. Self-explanatory but very *important.*

109. Self-explanatory.

110. Self-explanatory.

111. Self-explanatory.

112. Self-explanatory.

113. Self-explanatory.

114. Self-explanatory.

Item Inspected	Yes	No	N.A.	Comments
115. Are all accident prevention signs used to minimize workplace hazards? [.145(e)(e)]				
116. Are all exposed steam and hot water pipes within 7 ft of floor or working platform covered with an insulating material or guarded? [.264(e)(4)(iii)]				
117. At all loading docks employing powered industrial trucks, are wheel chocks used to prevent trailers or railroad cars from rolling? [.178(k)(1)]				
118. Is medical help readily available through personnel and first aid supplies approved by consulting physician? [.151(b)]				

115. Self-explanatory.

116. Self-explanatory.

117. Self-explanatory.

118. In the absence of an infirmary, clinic, or hospital in near proximity to the workplace that is used for treating all injured employees, a person or persons shall be adequately trained to render first aid. First aid supplies approved by the consulting physician shall be readily available.

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16. ABSTRACT

This handbook is addressed to laboratory directors, leaders of field investigations, and other personnel who bear responsibility for water and wastewater data. Subject matter of the handbook is concerned primarily with quality control (QC) for chemical and biological tests and measurements. Chapters are also included on QC aspects of sampling, microbiology, biology, radiochemistry, and safety as they relate to water and wastewater pollution control. Sufficient information is offered to allow the reader to inaugurate or reinforce programs of analytical QC that emphasize early recognition, prevention, and correction of factors leading to breakdowns in the validity of water and wastewater pollution control data.

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Water Analysis	Laboratory Services	
Laboratory Performance	Instrument Selection	07/B
Valid Data	Data Handling	
Analytical Quality Control	Skills and Training	

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APPENDIX 1

SAMPLERS AND SAMPLING PROCEDURES FOR HAZARDOUS WASTE STREAMS

by

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Grant No. R804692010

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DISCLAIMER

This report has been reviewed by the Municipal Environmental Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This study involved the development of simple but effective sampling equipment and procedures for collecting, handling, storing, and recording of hazardous wastes. A variety of sampling devices were developed and/or selected to meet the needs of those who regulate and manage hazardous wastes. Of particular importance is the development of the composite liquid waste sampler, the Coliwasa. The sampling procedures developed were designed to provide maximum protection for the sample collector, collection of representative samples of the bulk of wastes, and proper containment, identification, preservation, and handling of the samples.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

The goal of this project was to develop simple but effective sampling equipment and procedures for collecting, handling, storing, and recording samples of hazardous wastes. The report describes a variety of sampling devices designed to meet the needs of those who regulate and manage hazardous wastes. Particular emphasis is given to the development of a composite liquid waste sampler, the Coliwasa. This simple device is designed for use on liquid and semi-liquid wastes in a variety of containers, tanks, and ponds. Devices for sampling solids and soils are also described.

In addition to the sampling devices, the report describes procedures for development of a sampling plan, sample handling, safety precautions, proper recordkeeping and chain of custody, and sample containment, preservation, and transport. Also discussed are certain limitations and potential sources of error that exist in the sampling equipment and the procedures. The statistics of sampling are covered briefly, and additional references in this area are given.

This report was submitted in partial fulfillment of Research Grant No. R804692010 by the California Department of Health Services under sponsorship of the U.S. Environmental Protection Agency.

CONTENTS

FIGURES

TABLES

SECTION 1

INTRODUCTION

The growth in the size and complexity of industry and the implementation of air and waste pollution abatement technology has confronted the nation with the immensely difficult problem of managing large volumes of waste products that are often toxic, flammable, corrosive, and explosive. The problem is further exacerbated by the complexity of the waste. This difficult situation is now being addressed at many levels of government through a variety of regulatory agencies. Solution is being sought through a "cradle-to-grave" regulation of waste generation, transport, reprocessing, and disposal. Significant progress toward a solution is also being made by the private waste management industry with improved techniques in handling, resource recovery, and disposal.

The management of hazardous wastes may be addressed primarily as a chemical problem. With this approach, management decisions must be founded on proper knowledge of waste chemical compositions. Defining the information needed on waste composition to support management decisions presents an additional complication, for such information varies with waste type and with handling or disposal objectives. Regardless of the details, the required information results from chemical and physical testing of the waste.

Industrial waste predominantly occurs in volumes that are large enough to preclude testing or analysis of the entire body of the waste. Obtaining samples adequate in size for the required testing and representative of the bulk volumes of the wastes is therefore necessary. The obtainment of such representative samples presents special problem, for many wastes are complex, multiphase mixtures that vary greatly in viscosity, corrosivity, volatility, flammability, or capability to generate toxic gases.

This study was conducted to develop specialized equipment and procedures designed to handle the widest possible variety of waste sampling situations.

The equipment and procedures that have been developed and described in this report had their origins in the hazardous waste regulatory program of the California Department of Health Services. Early in this program, the necessity of reliable analytical data on waste composition became apprent. As a result, the problem of proper sampling of hazardous

wastes was addressed. Review of the wide variety of industrial wastes produced in California revealed that liquids or liquid-sludge mixtures accounted for the greatest volume of wastes. Most of these materials at some point are contained and/or transported in tank (vacuum) trucks or barrels. A primary concern, therefore, was to develop the capability for sampling these wastes.

The first prototype of a liquid waste sampler was the tube sampler, which was designated the composite liquid waste sampler or Coliwasa.[1] This sampling device, fabricated from readily available materials, was taken to the field and tested for its usability and reliability.

The first large-scale sampling of hazardous wastes was conducted jointly by the California Department of Health Services and the University of Southern California under the sponsorship of the U.S. Environmental Protection Agency (EPA)[2] In this sampling program, approximately 400 waste samples were collected. These samples varied greatly in composition and in physical characteristics.

Approximately 90% of all wastes sampled were liquids or sludges and could be sampled with the Coliwasa. The sampling program established the utility of this sampler. In addition, however, several deficiencies and needed improvments were demonstrated. Along with the need for liquid sampling equipment, a need was also demonstrated for simple but effective equipment for sampling solids, soils, and liquids in large tanks or ponds. This early study also clearly indicated the need for development of good safety procedures and sample handling, preservation, and custody procedures.

In November 1976, under a grant from the EPA, the California Department of Health Services embarked on a development program to establish recommended procedures and equipment for the sampling of hazardous wastes. Commercially available liquid samplers were investigated, but none was found to be adaptable to sampling hazardous wastes. Equipment development centered on the Coliwasa, which had been conceived and initially designed by waste management personnel of the Department. Solid, soil, and pond sampling equipment was obtained after an extensive review of the literature and testing of available equipment for efficiency. Criteria used in choosing candidate procedures were ready availability, reasonable cost, simplicity of design and operation, and chemical inertness. Candidate methods and samplers were subjected to laboratory and field tests. Laboratory tests for the liquid samplers consisted of sampling water as well as multiphase waste mixtures. The samplers were examined for leakage, ease of use and transfer, and cross contamination. In field tests, the samplers for liquids and solids were used on actual wastes existing in a variety of containers, ponds, or soils.

The body of the report gives detailed discussions of recommended samplers, preparation for sampling, sampling procedures, sample handling, and recordkeeping. The appendices present a variety of practical support data for the body of the report.

SECTION 2

CONCLUSIONS

The present study was designed to develop simple but effective sampling equipment for collecting represenative samples of hazardous wastes. In addition, recommended procedures for sample collection, handling, storage, and recording were to be developed. These primary objectives have been met, and the resulting sampling equipment and procedures are presented here.

The sampling equipment and procedures were designed to insure the widest possible applicability in the sampling of various types of hazardous wastes. The methods, however, are not intended to cover all possible sampling situations. Professional judgment on applicability must be exercised.

SECTION 3

RECOMMENDATIONS

The next step in the development of standardized sampling methods should be user verfication. Additional data on applicability, reliability, and other performance characteristics need to be developed before these recommended methods can become standard methods. This next phase will require considerable effort by a large number of collaborators, for the methodology described in this report is intended to be satisfactory for essentially the entire waste-producing industry. Significant benefit is to be gained by both industry and environmental regulatory agencies if efficient, reliable hazardous waste sampling methods can be established. We therefore strongly recommend that work on this validation begin immediately.

SECTION 4

SAMPLERS

Sampling of hazardous wastes requires different types of samplers. Some of these samplers are commercially available, but the others have to be fabricated. This section lists and describes suitable samplers. Their uses and commercial availability as well as directions for their use are reported. Directions for fabricating the commercially unavailable samplers are also outlined.

COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

The Coliwasa is the single most important hazardous waste sampler discussed in this report. It was chosen from a number of other liquid samplers, based on laboratory and field tests, as the most practical. It permits the representative sampling of multiphase wastes of a wide range of viscosity, corrosivity, volatility, and solids content. Its simple design makes it easy to use and allow the rapid collection of samples, thus minimizing the exposure of the sample collector to potential hazards from the wastes. The sampler is not commercially available, but it is relatively easy and inexpensive to fabricate. The cost of fabrication is low enough that the contaminated parts may be discarded after a single use when they cannot be easily cleaned.

The recommended model of the Coliwasa is shown in Figure 1. The history and development of this sampler is discussed in detail in Appendix A. The main parts of the Coliwasa consist of the sampling tube, the closure-locking mechanism, and the closure system.

The sampling tube consists of a 1.52-m(5-ft.) by 4.13-cm(1 5/8-in.) I.D. translucent plastic pipe, usually polyvinyl chloride (PVC) or borosilicate glass plumbing tube. The closure-locking mechanism consists of a short-length, channeled aluminum bar attached to the sampler's stopper rod by an adjustable swivel. The aluminum bar serves both as a T-handle and lock for the sampler's closure system. When the sampler is in the open position, the handle is place in the T-position and pushed down against the locking block. This manipulation pushes out the neoprene stopper and opens the sampling tube. In the close position, the handle is rotated until one leg of the T is squarely perpendicular against the locking block. This tightly seats the neoprene stopper against the bottom opening of the sampling tube and positively locks the sampler in the close position. The closure tension can be adjusted by shortening or lengthening the stopper rod by screwing it in or out

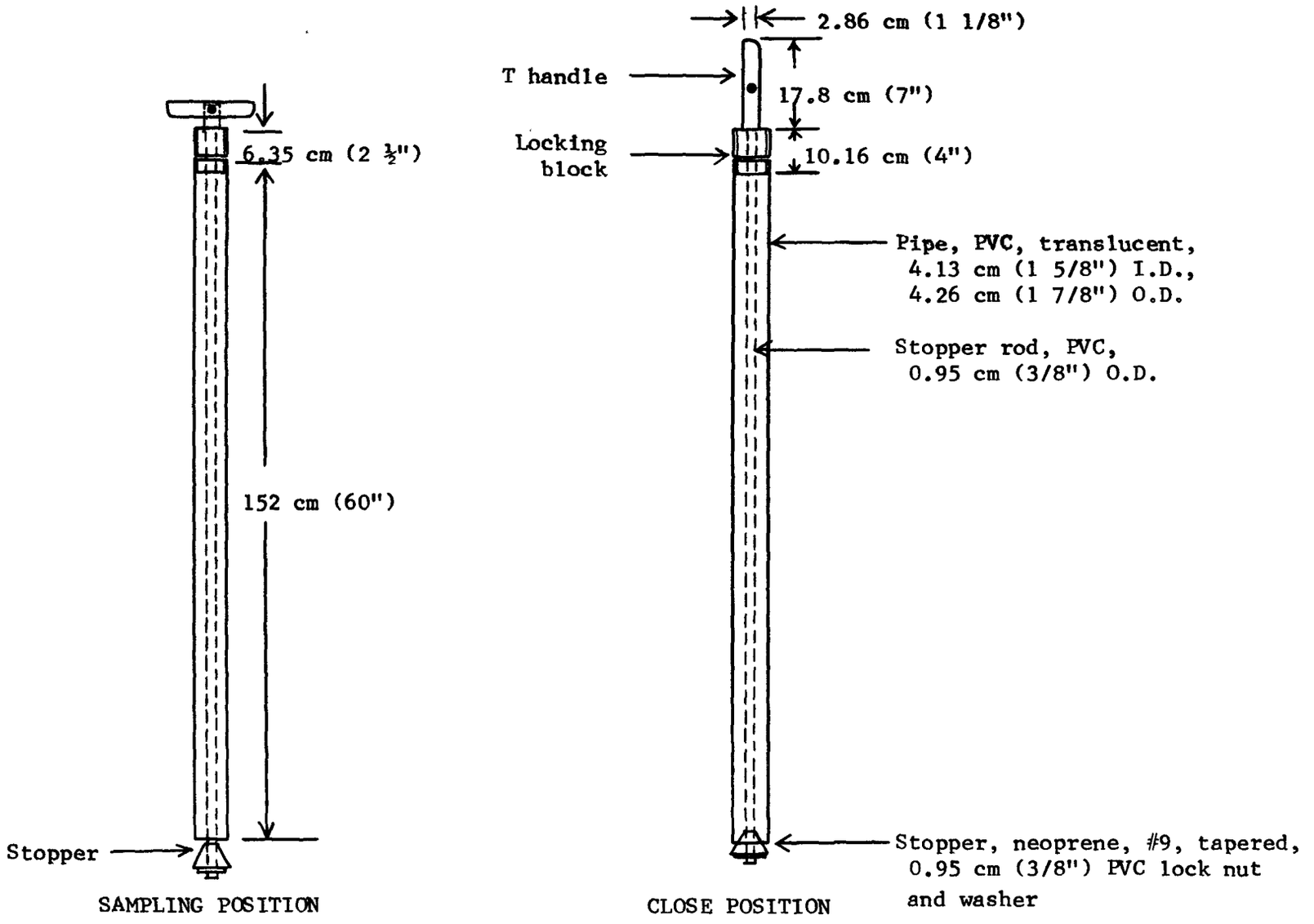


Figure 1. Composite liquid waste sampler (Coliwasa)

of the T-handle swivel. The closure system of the sampler consists of a sharply taped neoprene stopper attached to a 0.95-cm (3/8-in.) O.D. rod, usually PVC. The upper end of the stopper rod is connected to the swivel of the aluminum T-handle. The sharply tapered neoprene stopper can be fabricated according to specifications by plastic products manufacturers at an extremely high price, or it can be made in-house by grinding down the inexpensive stopper with a shop grinder as described in Note 1 of Appendix B.

Two types of Coliwasa samplers are made, namely plastic or glass. The plastic type consists of translucent plastic (usually PVC) sampling tube. The glass Coliwasa uses borosilicate glass plumbing pipe as the sampling tube and Teflon plastic stopper rod.

The complete list of parts for constructing the two types of Coliwasa samplers is given in Appendix B. The suppliers and approximate costs of the parts as well as the directions for fabricating the commercially unavailable parts are also given.

The sampler is assembled as shown in Figure 1 and as follows:

1. Attach the swivel to the T-handle with the 3.18 cm(1¼ in.) long bolt and secure with the 0.48 cm(3/16 in.) National Coarse(NC) washer and lock nut.

2. Attach the neoprene stopper to one end of the stopper rod and secure with the 0.95 cm(3/8 in.) washer and lock nut.

3. Install the stopper and stopper rod assembly in the sampling tube.

4. Secure the locking block sleeve on the block with glue or screws. This block can also be fashioned by shaping a solid plastic rod on a lathe to the required dimensions.

5. Position the locking block on top of the sampling tube such 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 hole of the block.

6. Attach the upper end of the stopper rod to the swivel of the T-handle.

7. Place the sampler in the close position and adjust the tension on the stopper by screwing the T-handle in or out.

Uses

The plastic Coliwasa is used to sample most containerized liquid wastes except wastes that contain ketones, nitrobenzene, dimethylforamide, mesityl oxide, and tetrahydrofuran.[3,4]

The glass Coliwasa is used to sample all other containerized liquid wastes that cannot be sampled with the plastic Coliwasa except strong alkali and hydrofluoric acid solutions.

Procedure for Use

1. Choose the plastic or glass Coliwasa for the liquid waste to be sampled and assemble the sampler as shown in Figure 1.

2. Make sure that the sampler is clean (see Section 5).

3. Check to make sure the sampler is functioning properly. Adjust the locking mechanism if necessary to make sure the neoprene rubber stopper provides a tight closure.

4. Wear necessary protective clothing and gear and observe required sampling precautions (see Section 6).

5. Put the sampler in the open position by placing the stopper rod handle in the T-position and pushing the rod down until the handle sits against the sampler's locking block.

6. Slowly lower the sampler into the liquid waste. (Lower the sampler at a rate that permits the levels of the liquid inside and outside the sampler tube to be about the same. If the level of the liquid in the sampler tube is lower than that outside the sampler, the sampling rate is too fast and will result in a nonrepresentative sample).

7. When the sampler stopper hits the bottom of the waste container, push the sampler tube downward against the stopper to close the sampler. Lock the sampler in the close position by turning the T handle until it is upright and one end rests tightly on the locking block.

8. Slowly withdraw the sampler from the waste container with one hand while wiping the sampler tube with a disposable cloth or rag with the other hand.

9. Carefully discharge the sample into a suitable sample container (see Section 6) by slowly opening the sampler. This is done by slowly pulling the lower end of the T handle away from the locking block while the lower end of the sampler is positioned in a sample container.

10. Cap the sample container; attach label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

11. Unscrew the T handle of the sampler and disengage the locking block. Clean sampler on site (see Section 5) or store the contaminated parts of the sampler in a plastic storage tube for subsequent cleaning. Store used rags in plastic bags for subsequent disposal.

12. Deliver the sample to the laboratory for analysis (see Section 6).

SOLID WASTE SAMPLERS

A number of tools are available for sampling solid substances. The most suitable of these for sampling hazardous solid wastes are the grain sampler, sampling trier, and the trowel or scoop.

Grain Sampler

The grain sampler (Figure 2) consists of two slotted telescoping tubes, usually made of brass or stainless steel. The outer tube has a conical, pointed tip on one end that permits the sampler to penetrate the material being sampled. The sampler is opened and closed by rotating the inner tube. Grain samplers are generally 61 to 100 cm (24 to 40 in.) long by 1.27 to 2.54 cm (½ to 1 in.) in diameter, and they are commercially available at laboratory supply houses.

Uses--

The grain sampler is used for sampling powdered or granular wastes or materials in bags, fiberdrums, sacks or similar containers. This sampler is most useful when the solids are no greater than 0.6 cm (¼ in.) in diameter.

Procedure for Use--

1. While the sampler is in the close position, insert it into the granular or powdered material or waste being sampled from a point near a top edge or corner, through the center, and to a point diagonally opposite the point of entry.[5]

2. Rotate the inner tube of the sampler into the open position.

3. Wiggle the sampler a few times to allow materials to enter the open slots.

4. Place the sampler in the close position and withdraw from the material being sampled.

5. Place the sampler in a horizontal position with the slots facing upward.

6. Rotate and slide out the outer tube from the inner tube.

7. Transfer the collected sample in the inner tube into a suitable sample container (see Section 6).

8. Collect two or more core samples at different points (see Section 6), and combine the samples in the same container.

9. Cap the sample container; attach label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

10. Clean (see Section 5) or store the sampler in plastic bag for subsequent cleaning.

11. Deliver the sample to the laboratory for analysis (see Section 6).

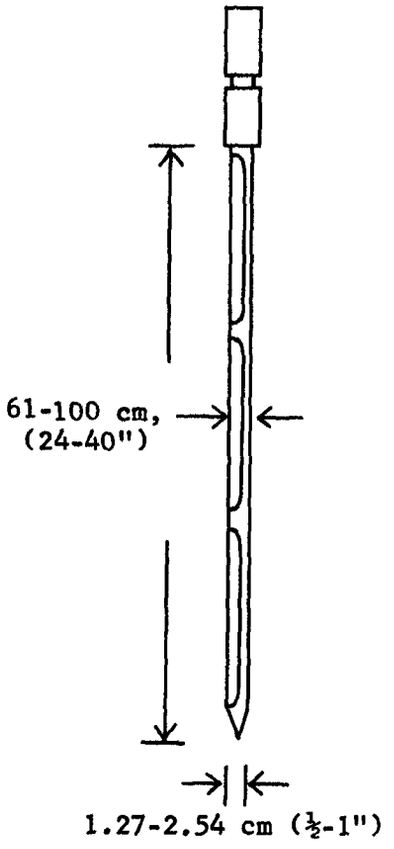


Figure 2. Grain sampler.

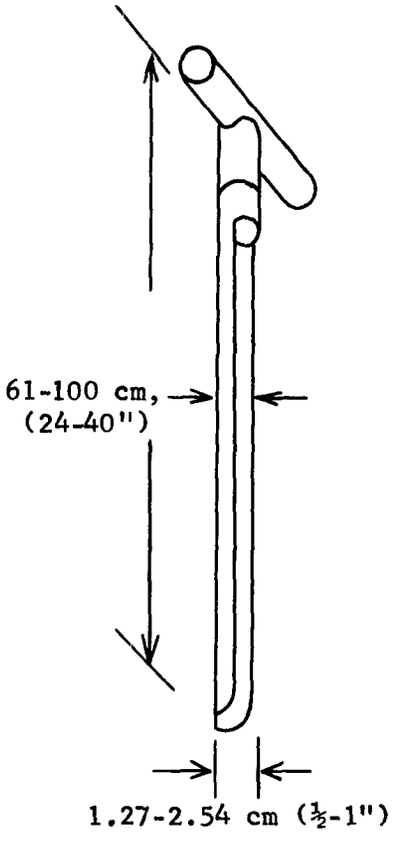


Figure 3. Sampling trier.

Sampling trier

A typical sampling trier (Figure 3) is a long tube with a slot that extends almost its entire length. The tip and edges of the tube slot are sharpened to allow the trier to cut a core of the material to be sampled when rotated after insertion into the material. Sampling triers are usually made of stainless steel with wooden handles. They are about 61 to 100 cm (24 to 40 in.) long and 1.27 to 2.54 cm (½ to 1 in.) in diameter. They can be purchased readily from laboratory supply houses.

Uses--

The use of the trier is similar to that of the grain sampler discussed above. It is preferred over the grain sampler when the powdered or

granular material to be sampled is moist or sticky.

In addition, the sampling trier can be used to obtain soft or loosened soil samples up to a depth of 61 cm(24 in.) as outlined below.

Procedure for Use--

1. Insert the trier into the waste material at a 0 to 45° angle from horizontal. This orientation minimizes the spillage of sample from the sampler. Extraction of samples might require tilting of the containers.

2. Rotate the trier once or twice to cut a core of material.

3. Slowly withdraw the trier, making sure that the slot is facing upward.

4. Transfer the sample into a suitable container (see Section 6) with the aid of a spatula and/or brush.

5. Repeat the sampling at different points (see Section 6). Two or more times and combine the samples in the same sample container.

6. Cap the sample container; attach the label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

7. Wipe the sampler clean, or store it in a plastic bag for subsequent cleaning.

8. Deliver the sample to the laboratory for analysis (see Section 6).

Trowel or Scoop

A garden-variety trowel looks like a small shovel (Figure 4). The blade is usually about 7 by 13 cm(3 by 5 in.) with a sharp tip. A laboratory scoop is similar to the trowel, but the blade is usually more curved and has a closed upper end to permit the containment of material. Scoops come in different sizes and makes. Stainless steel or polypropylene scoops with 7 by 15-cm(2 3/4 by 6-in.) blades are preferred. A trowel can be bought from hardware stores; the scoop can be bought from laboratory supply houses.

Uses--

An ordinary zinc-plated garden trowel can be used in some cases for sampling dry granular or powdered materials in bins or other shallow containers. The laboratory scoop, however, is a superior choice. It is usually made of materials less subject to corrosion or chemical reactions, thus lessening the probability of sample contamination.

The trowel or scoop can also be used in collecting top surface soil samples.

Procedure for Use--

1. At regular intervals (see Section 6), take small, equal portions of sample from the surface or near the surface of the material to be sampled.

2. Combine the samples in a suitable container (see Section 6).

3. Cap the container; attach the label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

4. Deliver the sample to the laboratory for analysis (see Section 6).

SOIL SAMPLERS

There is a variety of soil samplers used. For taking soil core samples, the scoop, sample trier, soil auger, and Veihmeyer sampler can be used. These samplers are commercially available and relatively inexpensive.

Scoop or Trowel

See the preceding section on solid waste samplers for the description of a scoop or trowel (Figure 4).

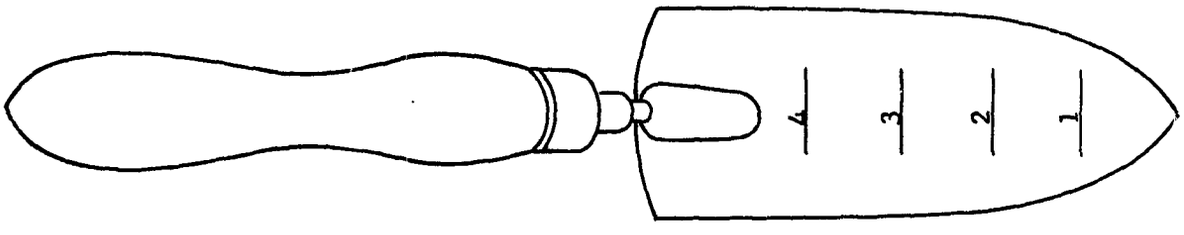


Figure 4. Trowel or scoop with calibrations.

Uses--

The scoop is used to collect soil samples up to 8 cm(3 in.) deep. It is simple to use, but identical mass sample units for a composite sample are difficult to collect with this sampler. The procedure for use of the scoop is outlined in the preceding section on solid waste samplers.

Sampling Trier

See the preceding section on solid waste samplers for the description of a sampling trier (Figure 3).

Uses--

This sampler can be used to collect soil samples at a depth greater than 8 cm(3 in.). The sampling depth is determined by the hardness and types of soil being sampled. This sampler can be difficult to use in stony, dry, very heavy, or sandy soil. The collected sample tends to be slightly compacted, but this method permits observation of the core sample before removal.[6]

Procedure for Use--

Procedure for use of the sampling trier can be found in the section on solid waste samplers.

Soil Auger

This tool consists of a hard metal central shaft and sharpened spiral blades (Figure 5). When the tool is rotated clockwise by its wooden T handle, it cuts the soil as it moves forward and discharges most of the loose soil upward. The cutting diameter is about 5 cm(2 in.). The length is about 1 m(40 in.), with graduations every 15.2 cm(6 in.). The length can be increased up to 2 m(80 in.). This tool can be bought from stores and, in some cases, from laboratory supply houses.

Uses--

The auger is particularly useful in collecting soil samples at depths greater than 8 cm(3 in.). This sampler destroys the structure of cohesive soil and does not distinguish between samples collected near the surface or toward the bottom. It is not recommended, therefore, when an undisturbed soil sample is desired.

Procedure for Use--

1. Select the sampling point (see Section 6) and remove unnecessary rocks, twigs, and other non-soil materials.

2. Install the sampler's wooden T handle in its socket.

3. Bore a hole through the middle of an aluminum pie pan large enough to allow the blades of the auger to pass through. The pan will be used to catch the sample brought to the surface by the auger.

4. Spot the pan against the selected sampling point.

5. Start augering through the hole in the pan until the desired sampling depth is reached.

6. Back off the auger and transfer the sample collected in the catch pan and the sample adhering to the auger to a suitable container (see Section 6). Spoon out the rest of the loosened sample with a sampling trier.

7. Repeat the sampling at different sampling points (see Section 6), and combine the samples in the same container as in step 6.

8. Cap the sample container; attach label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

9. Brush off and wipe the sampler clean, or store it in a plastic bag for subsequent cleaning.

10. Deliver the sample to the laboratory for analysis (see Section 6).

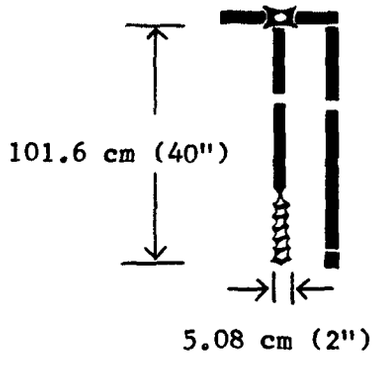


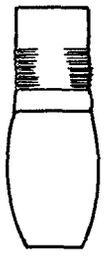
Figure 5. Soil auger.

A. Drive hammer

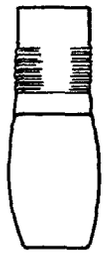
B. Head

C. Tube

D. Point



Standard point

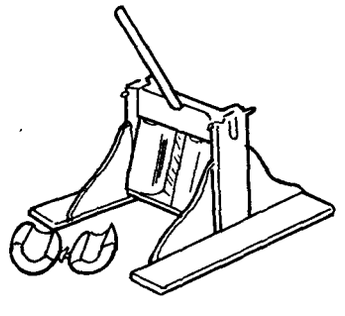


Constricted point

Bulge point

Special point

Point types



Puller jack and grip

Figure 6. Veihmeyer sampler

Veihmeyer Soil Sampler

This sampler was developed by Professor F.J. Veihmeyer of the University of California in Davis.[7] The parts of a basic sampler and the corresponding costs are given in Table 1, and the basic sampler is shown in Figure 6.

TABLE 1. BASIC PARTS AND COSTS OF A VEIHMEYER SOIL SAMPLER

Part[a]	Cost[b]
Tube, 1.5 m (5 ft.)	$ 50.40
Tube, 3 m (10 ft.)	84.75
Tip, type A, general use	25.80
Drive head	29.05
Drop hammer, 6.8 kg (15 lb.)	71.85
Puller jack and grip[c]	161.90
Total	$ 433.75

[a] Only one of each part is needed. They are manufactured by Hansen Machine Works, 334 N. 12th Street, Sacramento, CA 95815.

[b] Based on August 1, 1977, price list.

[c] Recommended for deep soil sampling.

The tube is chromium-molybdenum steel and comes in various standard lengths from 0.91 to 4.9 m(3 to 16 ft.) and calibrated every 30.48 cm(12 in.). Longer tubes can be obtained on special order. Different points (Figure 6) are also available for different types of soil and sampling. Each point is shaped to penetrate specific types of soil without pushing the soil ahead of it, thus preventing the core from compacting in the tube. The standard point is adequate for most general sampling purposes. The inside taper of each point is designed to keep the sample from being sucked out of the tube as it is pulled from the ground. The drive head protects the top of the tube from deforming when the tube is driven into the ground with the drive hammer. The hammer doubles as a drive weight and handle when pulling the sampler from the ground. When the sampler tube cannot be pulled easily from the ground, a special puller jack and grip

are also available. Specifications for the various parts of the Veihmeyer sampler are given as follows:

Points	Chrome-molly steel, heat-treated. Includes a standard point for general use, a constricted point for deep sampling in heavy clay (keeps core from being sucked out of the tube), a bulge point for shallow sampling in heavy clay, and a special point for dry sand. (See Figure 6D).
Drive hammer . .	Standard weight is 6.8 kg (15 lb.). (See Figure 6A)
Tubes . .	Chrome-molly steel. Maximum length is 4.9 m (16 ft.). (See Figure 6C).
Head . .	Chrome-molly steel, heat-treated. (See Figure 6B).
Puller jack . .	Cast aluminum frame with steel roller assembly and handle.
Grip . .	Chrome-molly steel, heat-treated.

Uses--

The Veihmeyer sampler is recommended for core sampling of most types of soil. It may not be applicable to sampling stony, rocky, or very wet soil.

Procedure for Use--

1. Assemble the sampler by screwing in the tip and the drive head on the sampling tube.

2. Insert the tapered handle (drive guide) of the drive hammer through the drive head.

3. Place the sampler in a perpendicular position on the soil to be sampled.

4. With the left hand holding the tube, drive the sampler into the ground to the desired sampling depth by pounding the drive head with the drive hammer. Do not drive the tube further than the tip of the hammer's drive guide.

5. Record the length of the tube that penetrated the ground.

6. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.

7. Rotate the sampler at least two revolutions to shear off the sample at the bottom.

8. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head and rotate about 90°.

9. Withdraw the sampler from the ground by pulling the handle (hammer) upwards. When the sampler cannot be withdrawn by hand, as in deep soil sampling, use the puller jack and grip.

10. Dislodge the hammer from the sampler; turn the sampler tube upside down; tap the head gently against the hammer; and carefully recover the sample from the tube. The sample should slip out easily.

11. Store the core sample, preferably, in a rigid, transparent, or translucent plastic tube when observation of soil layers is to be made. The use of the tube will keep the sample relatively undisturbed. In other cases, use a 1000-or 2000-ml (1-qt. or ½-gal) sample container (see Section 6) to store the sample.

12. Collect additional core samples at different points (see Section 6).

13. Label the samples; affix the seals; record in the field log book; complete analysis request sheet and chain of custody record; and deliver the samples to the laboratory for analysis (see Section 6).

Waste Pile Sampler

A waste pile sampler (Figure 7) is essentially a large sampling trier. It is commercially available, but it can be easily fabricated from sheet metal plastic pipe. A polyvinyl chloride plumbing pipe 1.52 m(5 ft) long by 3.2 cm(1¼ in.) I.D. by 0.32 cm(1/8 in.) wall thickness is adequate. The pipe is sawed lengthwise (about 60/40 split) until the last 10 cm(4 in.) The narrower piece is sawn off and hence forms a slot in the pipe. 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. The plastic pipe can be purchased from hardware stores.

Uses--

The waste pile sampler is used for sampling wastes in large heaps with cross-sectional diameters greater than 1 m(39.4 in.). It can also be used for sampling granular or powdered wastes or materials in large bins, barges, or silos where the grain sampler or sampling trier is not long enough. This sampler does not collect representative samples when the diameters of the solid particles are greater than half the diameter of the tube.

Procedure for Use--

1. Insert the sampler into the waste material being sampled at 0 to 45° from horizontal.

2. Rotate the sampler two or three times in order to cut a core of the material.

3. Slowly withdraw the sampler, making sure that the slot is facing upward.

4. Transfer the sample into a suitable container (see Section 6) with the aid of a spatula and/or brush.

5. Repeat the sampling at different sampling points (see Section 6) two or more times and combine the samples in the same sample container in step 4.

6. Cap the container; attach label and seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

7. Wipe the sampler clean or store it in a plastic bag for subsequent cleaning.

8. Deliver the sample to the laboratory for analysis (see Section 6).

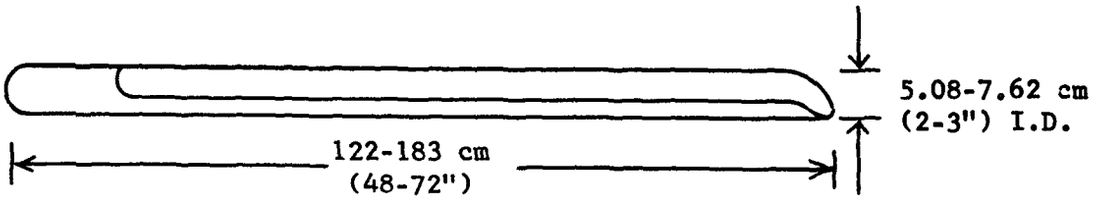


Figure 7. Waste pile sampler.

Pond Sampler

The pond sampler (Figure 8) consists of an adjustable clamp attached to the end of a two or three piece telescoping aluminum tube that serves as the handle. The clamp is used to secure a sampling beaker. The sampler is not commercially available, but it is easily and inexpensively fabri-

cated. The tubes can be readily purchased from most hardware or swimming pool supply stores. The adjustable clamp and sampling beaker can be obtained from most laboratory supply houses. The materials required to fabricate the sampler are given in Table 2.

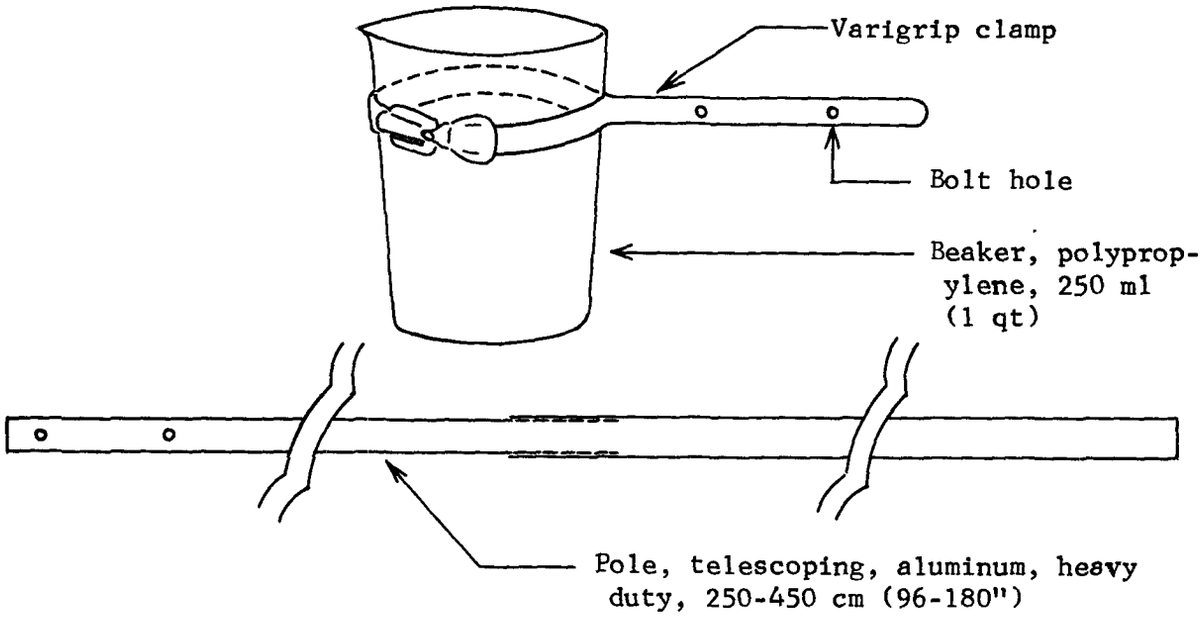


Figure 8. Pond sampler.

TABLE 2. BASIC PARTS AND APPROXIMATE COSTS OF A POND SAMPLER

Quantity	Item	Supplier	Approximate Cost
1	Clamp, adjustable, 6.4 to 8.9 cm(2½ to 3½ in.) for 250-to 600-ml(½ to 1½-pt.) beakers	Laboratory supply houses	$ 7.00
1	Tube, aluminum, heavy duty, telescoping extends 2.5 to 4.5 m(8 to 15 ft.) with joint cam locking mechanism. Pole diameters 2.54 cm(1 in.) I.D. and 3.18 cm(1¼ in.) I.D.	Olympic Swimming Pool Co. 807 Buena Vista Street, Alameda, Calif. 94501 or other general swimming pool supply houses.	16.24
1	Beaker, polypropylene, 250-ml(½ pt.)	Laboratory supply houses.	1.00
4	Bolts, 6.35 by 0.64 cm(2¼ by ¼ in.) NC	Hardware stores	.20
4	Nuts, 0.64 cm(¼ in.) NC	Hardware stores	.20
	Total		$24.64

Uses--

The pond sampler is used to collect liquid waste samples from disposal ponds, pits, lagoons, and similar reservoirs. Grab samples can be obtained at distances as far as 3.5 m(11½ ft) from the edge of the ponds. The tubular aluminum handle may bow when sampling very viscous liquids if sampling is not done slowly.

Procedure for Use--

1. Assemble the pond sampler. Make sure that the sampling beaker and the bolts and nuts that secure the clamp to the pole are tightened properly.

2. With proper protective garment and gear (see Section 6), take grab samples from the pond at different distances and depths (see Section 6).

3. Combine the samples in one suitable container (see Section 6).

4. Cap the container; label and affix the seal; record in field log book; and complete sample analysis request sheet and chain of custody record.

5. Dismantle the sampler; wipe the parts with terry towels or rags and store them in plastic bags for subsequent cleaning. Store used towels or rags in garbage bags for subsequent disposal.

6. Deliver the sample to the laboratory for analysis (see Section 6).

Weighted Bottle Sampler

This sampler (Figure 9) consists of a bottle, usually glass, a weight sinker, a bottle stopper, and a line that is used to open the bottle and to lower and raise the sampler during sampling. There are a few variations of this sampler, as illustrated in the ASTM Methods D 270[8] and E 300[9]. The ASTM sampler, which uses a metallic bottle basket that also serves as weight sinker, is preferred. The weighted bottle sampler can either be fabricated or purchased.

Uses--

The weighted bottle sampler can be used to sample liquids in storage tanks, wells, sumps, or other containers that cannot be adequately sampled with a Coliwasa. The sampler cannot be used to collect liquids that are incompatible or that react chemically with the weight sinker and line.

Procedure for use--

1. Assemble the weighted bottle sampler as shown in Figure 9.

2. Using protective sampling equipment, in turn, lower the sampler to proper depths to collect the following samples:

   a) upper sample - middle of upper third of tank contents.
   b) middle sample - middle of tank contents.
   c) lower sample - near bottom of tank contents.

3. Pull out the bottle stopper with a sharp jerk of the sampler line.

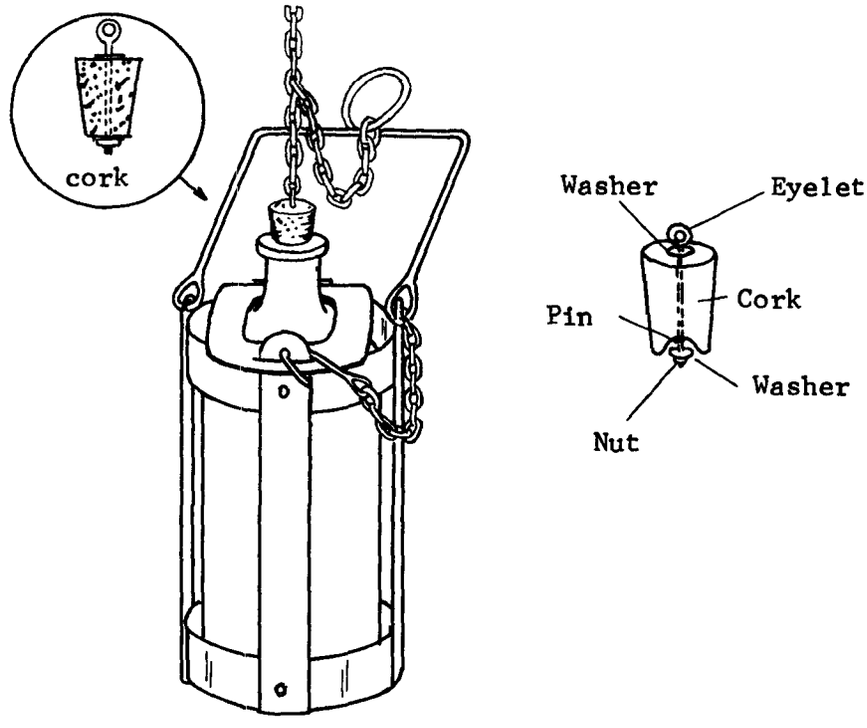
4. Allow the bottle to fill completely, as evidence by the cessation of air bubbles.

5. Raise the sampler and retrieve and cap the bottle. Wipe off the outside of the bottle with a terry towel or rag. The bottle can serve as the sample container.

6. Label each of the three samples collected; affix seal; fill out sample analysis request sheet and chain of custody record; record in the field log book.

7. Clean onsite or store contaminated sampler in a plastic bag for subsequent cleaning.

8. Deliver the sample to the laboratory for analysis (see Section 6). Instruct the laboratory to perform analysis on each sample or a composite of the samples.



1000-ml (1-quart) weighted bottle catcher

Figure 9. Weighted bottle sampler.

SECTION 5

PREPARATION FOR SAMPLING

GENERAL CONSIDERATIONS

Adequate preparation for sampling is necessary to perform proper sampling of any hazardous waste. A checklist of items required for field sampling helps to ensure proper preparation. Such a checklist is given in Appendix C. The appendix lists the minimal equipment, accessories, and supplies necessary to sample any type of solid or liquid waste. When the type of waste to be sampled is known beforehand, the list can be narrowed down to the actual pieces of equipment to be used.

When sample analyses are to be performed in the field, such as for pH, flammability, or explosivity, then the necessary apparatus for such tests should also be included in the preparation for sampling.

CLEANING AND STORAGE OF SAMPLER

All samplers must be clean before use. Used samplers must be washed with warm detergent solution (i.e., Liquinox or Alconox), rinsed several times with tap water, rinsed with distilled water, drained of excess water, and air dried or dried with a stream of warm, dry air or wiped dry. For samplers that have been used to sample petroleum products and oil residues, it may be necessary first to wipe the samplers with absorbent cloth to eliminate the residues. The equipment is then rinsed with an organic solvent such as petroleum naphtha or trichloroethane, followed by washing with the detergent solution and rinsing with water. A necessary piece of equipment for cleaning the tube of a Coliwasa is a bottle brush that fits tightly the inside diameter of the tube. The brush is connected to a rod of sufficient length to allow for reaching the entire length of the sampler tube. Using this ramrod and fiber-reinforced paper towels, the Coliwasa tube may be quickly cleaned.

Improper cleaning of sampling equipment will cause cross contamination of samples. Such contamination is of particular importance in samples taken for legal or regulatory purposes. Also, contamination becomes important when sampling wastes from different production sources within the same time frame. A detailed study of cross contamination as a function of cleaning procedures has not been carried out. A recommended policy is that if samples are to be taken for legal or regulatory purposes, or if analysis is to be performed on samples expected to contain low-level (low ppm range)

concentrations of hazardous components, that a fresh, unused sampler be used. The Coliwasa in particular was designed to be semidisposable. Parts of the device that become contaminated during sampling (i.e., the tube, the stopper rod, and the stopper mechanism) may be discarded at little expense. In addition, or these parts may later be disassembled, secured, and returned to the laboratory for thorough decontamination and reused.

If the cleaning process has the potential for producing toxic fumes, ensure adequate ventilation. If the washings are hazardous, store them in closed waste containers and dispose of them properly in approved disposal sites. Locations of these sites close to one's area may be obtained by calling the agency in the State responsible for the regulation of hazardous wastes. Store the clean samplers in a clean and protected area. Polyethylene plastic tubes or bags are usually adequate for storing the samplers.

SECTION 6

SAMPLING PROCEDURES

PURPOSES AND GENERAL CONSIDERATIONS

Sampling of hazardous wastes is conducted for different purposes. In most instances, it is performed to determine compliance with existing regulations promulgated by the different regulatory agencies. In some cases, it is conducted to obtain data for purposes of classifying, treating, recovering, recycling, or determining compatibility characteristics of the wastes. Sampling is also conducted as an important part of research activities.

In general, sampling of hazardous wastes requires the collection of adequate sized, representative samples of the body of wastes. Sampling situations vary widely and therefore no universal sampling procedure can be recommended. Rather, several procedures are outlined for sampling different types of wastes in various states and containers.

These procedures require a plan of action to maximize safety of sampling personnel, minimize sampling time and cost, reduce errors in sampling, and protect the integrity of the samples after sampling. The following steps are essential in this plan of action:

1. Research background information about the waste.
2. Determine what should be sampled.
3. Select the proper sampler.
4. Select the proper sample container and closure.
5. Design an adequate sampling plan that includes the following:
   a) Choice of the proper sampling point.
   b) Determination of the number of samples to be taken.
   c) Determination of the volumes of samples to be taken.
6. Observe proper sampling precautions.
7. Handle samples properly.
8. Identify samples and protect them from tampering.
9. Record all sample information in a field notebook.
10. Fill out chain of custody record.
11. Fill out the sample analysis request sheet.
12. Deliver or ship the samples to the laboratory for analysis.

BACKGROUND INFORMATION ABOUT THE WASTE

Accurate background information about the waste to be sampled is very important in planning any sampling activity. The information is used to determine the types of protective sampling equipment to be used, sampling precautions to be observed, as well as the types of samplers, sample containers, container closures, and preservatives (when needed) required. Generally, the information about the waste determines the kind of sampling scheme to be used.

Most often, the information about the waste is incomplete. In these instances, as much information as possible must be obtained by examining any documentation pertaining to the wastes, such as the hauler's manifest (Figure 10). When documentation is not available, information may be obtained from the generator, hauler, disposer, or processor. The information obtained is checked for hazardous properties against references such as the Dangerous Properties of Industrial Materials,[10] the Merck Index,[3] the Condensed Chemical Dictionary,[11] Toxic and Hazardous Industrial Chemicals Safety Manual for Handling and Disposal with Toxicity and Hazardous Data,[12] or other chemical references.

SELECTION OF SAMPLER

Hazardous wastes are usually complex, multiphase mixtures of liquids, semisolids, sludges, or solids.[1] The liquid and semisolid mixtures vary greatly in viscosity, corrosivity, volatility, explosivity, and flammability. The solid wastes can range from powders to granules to big lumps. The wastes are contained in drums, barrels, sacks, bins, vacuum trucks, ponds, and other containers. No single type of sampler can therefore be used to collect representative samples of all types of wastes. Table 3 lists most waste types and the corresponding recommended samplers to be used.

SELECTION OF SAMPLE CONTAINER, CONTAINER CLOSURE, AND CLOSURE LINING

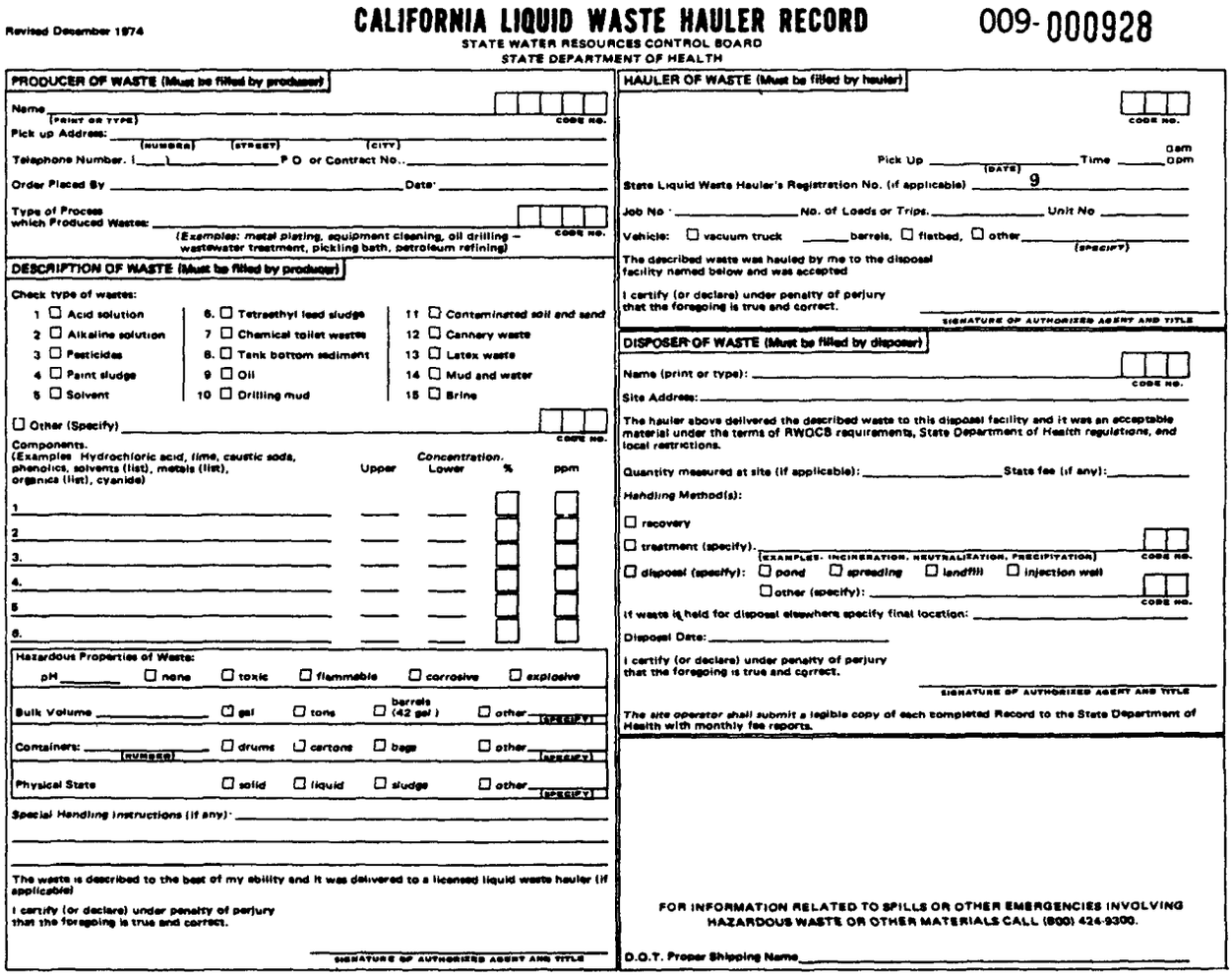
Containers

The most important factors to consider when choosing containers for hazardous waste samples are compatibility, resistance to breakage, and volume. Containers must not melt, rupture, or leak as a result of chemical reactions with constituents of waste samples. Thus, it is important to have some idea of the components 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 required volume of samplers or the entire volume of a sample contained in samplers.

Plastic and glass containers are generally used for collection and storage of hazardous waste samples. Commonly available plastic containers

are made of high-density or linear polyethylene (LPE), conventional polyethylene, polypropylene, polycarbonate, teflon FEP (fluorinated ethylene propylene), polyvinyl chloride (PVC), or polymethylpentene. Teflon FEP is the most inert plastic, but LPE offers the best combination of chemical resistance and low cost.

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 the cheapest and most readily available. Borosilicate such as Pyrex and Corex glass containers are also commercially available, but they are expensive and not always readily obtainable. Glass containers are breakable and much heavier than plastic containers.



Revised December 1974

CALIFORNIA LIQUID WASTE HAULER RECORD 009-000928

STATE WATER RESOURCES CONTROL BOARD
STATE DEPARTMENT OF HEALTH

PRODUCER OF WASTE (Must be filled by producer)

Name _____ (PRINT OR TYPE) CODE NO.

Pick up Address: _____ (NUMBER) (STREET) (CITY)

Telephone Number. ( ) _____ P O or Contract No.. _____

Order Placed By _____ Date _____

Type of Process which Produced Wastes: _____ CODE NO.

(Examples: metal plating, equipment cleaning, oil drilling – wastewater treatment, pickling bath, petroleum refining)

DESCRIPTION OF WASTE (Must be filled by producer)

Check type of wastes:

1 ☐ Acid solution	6. ☐ Tetraethyl lead sludge	11 ☐ Contaminated soil and sand
2 ☐ Alkaline solution	7 ☐ Chemical toilet wastes	12 ☐ Cannery waste
3 ☐ Pesticides	8. ☐ Tank bottom sediment	13 ☐ Latex waste
4 ☐ Paint sludge	9 ☐ Oil	14 ☐ Mud and water
5 ☐ Solvent	10 ☐ Drilling mud	15 ☐ Brine

☐ Other (Specify) _____ CODE NO.

Components. (Examples Hydrochloric acid, lime, caustic soda, phenolics, solvents (list), metals (list), organics (list), cyanide)	Concentration. Upper	Lower	%	ppm
1				
2				
3.				
4.				
5				
6.				

Hazardous Properties of Waste:

pH _____ ☐ none ☐ toxic ☐ flammable ☐ corrosive ☐ explosive

Bulk Volume _____ ☐ gal ☐ tons ☐ barrels (42 gal) ☐ other _____ (SPECIFY)

Containers: _____ (NUMBER) ☐ drums ☐ cartons ☐ bags ☐ other _____ (SPECIFY)

Physical State ☐ solid ☐ liquid ☐ sludge ☐ other _____ (SPECIFY)

Special Handling Instructions (if any): _____

The waste is described to the best of my ability and it was delivered to a licensed liquid waste hauler (if applicable)

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

_____ SIGNATURE OF AUTHORIZED AGENT AND TITLE

HAULER OF WASTE (Must be filled by hauler)

CODE NO.

Pick Up _____ (DATE) Time _____ ☐am ☐pm

State Liquid Waste Hauler's Registration No. (if applicable) 9 _____

Job No _____ No. of Loads or Trips. _____ Unit No _____

Vehicle: ☐ vacuum truck _____ barrels, ☐ flatbed, ☐ other _____ (SPECIFY)

The described waste was hauled by me to the disposal facility named below and was accepted

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

_____ SIGNATURE OF AUTHORIZED AGENT AND TITLE

DISPOSER OF WASTE (Must be filled by disposer)

Name (print or type): _____ CODE NO.

Site Address: _____

The hauler above delivered the described waste to this disposal facility and it was an acceptable material under the terms of RWQCB requirements, State Department of Health regulations, and local restrictions.

Quantity measured at site (if applicable): _____ State fee (if any): _____

Handling Method(s):

☐ recovery

☐ treatment (specify). _____ (EXAMPLES: INCINERATION, NEUTRALIZATION, PRECIPITATION) CODE NO.

☐ disposal (specify): ☐ pond ☐ spreading ☐ landfill ☐ injection well

☐ other (specify): _____ CODE NO.

If waste is held for disposal elsewhere specify final location: _____

Disposal Date: _____

I certify (or declare) under penalty of perjury that the foregoing is true and correct.

_____ SIGNATURE OF AUTHORIZED AGENT AND TITLE

The site operator shall submit a legible copy of each completed Record to the State Department of Health with monthly fee reports.

FOR INFORMATION RELATED TO SPILLS OR OTHER EMERGENCIES INVOLVING HAZARDOUS WASTE OR OTHER MATERIALS CALL (800) 424-9300.

D.O.T. Proper Shipping Name _____

Figure 10. Example of waste manifest

TABLE 3. SAMPLERS RECOMMENDED FOR VARIOUS TYPES OF WASTE

Waste type	Recommended sampler	Limitations
Liquids, sludges, and slurries in drums, vacuum trucks, barrels, and similar containers	Coliwasa	Not for containers 1.5 m(5 ft) deep.
	a) Plastic	Not for wastes containing ketones, nitrobenzene, dimethylformamide, mesityl oxide, or tetrahydrofuran[3,4].
	b) Glass	Not for wastes containing hydrofluoric acid and concentrated alkali solutions.
Liquids and sludges in ponds, pits, or lagoons	Pond	Cannot be used to collect samples beyond 3.5 m(11.5 ft). Dip and retrieve sampler slowly to avoid bending the tubular aluminum handle.
Powdered or granular solids in bags, drums, barrels, and similar containers	a) Grain sampler	Limited application for sampling moist and sticky solids with a diameter 0.6 cm(¼ in.).
	b) Sampling trier	May incur difficulty in retaining core sample of very dry granular materials during sampling.
Dry wastes in shallow containers and surface soil	Trowel or scoop	Not applicable to sampling deeper than 8 cm(3 in.). Difficult to obtain reproducible mass of samples.
Waste piles	Waste pile sampler	Not applicable to sampling solid wastes with dimensions greater than half the diameter of the sampling tube.
Soil deeper than 8 cm(3 in.)	a) Soil auger	Does not collect undisturbed core sample.
	b) Veihmeyer sampler	Difficult to use on stony, rocky, or very wet soil.
Wastes in storage tanks	Weighted bottle sampler	May be difficult to use on very viscous liquids.

Wide-mouth 1000-and 2000-ml(1 qt-and ½-gal.) glass bottles are recommended for waste samples containing petroleum distillates, chlorinated hydrocarbons, pesticides, and petroleum residues that are mostly incompatible with plastic containers. For all other types of samples, 1000-and 2000-ml(1-qt and ½-gal.) wide-mouth LPE bottles are recommended.

Container Closures and Closure Linings

The containers must have tight, screw-type lids. Plastic bottles are usually provided with screw caps made of the same material as the bottles. No cap liners are usually required. Glass containers usually come with glass or rigid plastic screw caps such as Bakelite. The plastic caps are popularly provided with waxed paper liners. Other liner materials are polyethylene, polypropylene, neoprene, and Teflon FEP plastics. For containing hazardous waste samples requiring petroleum distillates, chlorinated hydrocarbons, pesticides, and petroleum residue analyses. Bakelite caps with Teflon liners are recommended to be used with glass bottles. Teflon liners may be purchased from plastic specialty supply houses (e.g., Scientific Specialties Service, Inc., P.O. Box 352, Randallstown, Md. 21133).

Table 4 shows most types of wastes and the corresponding sampling containers and closures recommended.

SAMPLING PLAN

The sampling plan should be well formulated before any actual sampling is attempted. The plan must be consistent with the objectives of the sampling. It must include the selected point(s) of sampling and the intended number, volumes, and types (i.e., composite, grab, etc.) of samples to be taken. These requirements are discussed below.

POINT OF SAMPLING

A representative sample is crucial to the sampling plan. This sample depends on proper selection of sampling points in the bulk of the waste. Hazardous wastes are usually multiphase mixtures and are contained and stored in containers of different sizes and shapes. No single sampling point can be specified for all types of containers. Table 5 lists most types of containers used for hazardous wastes and the corresponding recommended sampling points.

NUMBER OF SAMPLES

The number of samples to be taken primarily depends on the information desired. Table 6 lists the recommended number of samples to be collected consistent with the information sought and the types of wastes to be sampled. In hazardous waste management, the properties and the average concentrations of the hazardous components are usually desired. In this

TABLE 4. SAMPLE CONTAINERS AND CLOSURES RECOMMENDED FOR VARIOUS TYPES OF WASTE

Waste type item	Recommended container	Recommended closure
Oil wastes except pesticides, HC, chlorinated HC, and photosensitive wastes	Linear polyethylene (LPE) bottles,[a] 1000-and 2000-ml(1-qt. and ½-gal.), wide mouth	LPE caps
Pesticides, HC, and chlorinated HC	Glass bottles,[b] wide-mouth, 1000-and 2000-ml (1-qt. and ½-gal.).	Bakelite caps with Teflon liner[c]
Photosensitive wastes	Amber LPE or brown glass[d] bottles, wide-mouth, 1000-and 200-ml (1-qt. and ½-gal.)	LPE caps for the LPE bottles; Bakelite caps with Teflon liner for the glass bottles

[a]Nalgene, Cat. Nos. 2104-0032 and 2120-0005, or equivalent.

[b]Scientific Products, Cat. Nos. 87519-32 and B7519-64, or equivalent.

[c]Available from Scientific Specialities, P.O. Box 352, Randallstown, Md.

[d]Scientific Products, Cat. Nos. B7528-050 and 7528-2L, or equivalent.

TABLE 5. SAMPLING POINTS RECOMMENDED FOR MOST WASTE CONTAINERS

Container type	Sampling point
Drum, bung on one end	Withdraw sample through the bung opening.
Drum, bung on side	Lay drum on side with bung up. Withdraw sample through the bung opening.
Barrel, fiberdrum, buckets, sacks, bags	Withdraw samples through the top of barrels, fiberdrums, buckets, and similar containers. Withdraw samples through fill openings of bags and sacks. Withdraw samples through the center of the containers and to different points diagonally opposite the point of entry.
Vacuum truck and similar containers	Withdraw sample through open hatch. Sample all other hatches.
Pond, pit, lagoons	Divide surface area into an imaginary grid.[a] Take three samples, if possible: one sample near the surface, one sample at mid-depth or at center, and one sample at the bottom. Repeat the sampling at each grid over the entire pond or site.
Waste pile	Withdraw samples through at least three different points near the top of pile to points diagonally opposite the point of entry.
Storage tank	Sample from the top through the sampling hole.
Soil	Divide the surface area into an imaginary grid.[a] Sample each grid.

[a]The number of grid is determined by the desired number of samples to be collected, which when combined should give a representative sample of the wastes.

respect, collecting one representative sample of a given waste is usually adequate. This sample can either be collected from a single sampling point with a composite sampler, or several samples can be collected from various sampling points and combine into one composite sample.

When gathering evidence for possible legal actions, multiple samples of a waste are usually collected. Three identical samples are desirable: one sample is given to the company or organization responsible for the waste, the second sample is submitted to the laboratory for analysis, and the third sample is kept in storage for possible use as a referee sample. Subdividing a waste sample is not recommended unless it is homogeneous.

VOLUME OF SAMPLES

Sufficient volume of a sample, representative of the main body of the waste, must be collected. This sample must be adequate in size for all needs, including laboratory analysis, splitting with other organizations involved, etc. In collecting liquid waste samples in drums, vacuum trucks, or similar containers, the volume collected in the Coliwasa usually determines the volume of the sample. This volume can range from 200 to 1800 (½ pt. to 1.9 qt.). In most cases, 1000 ml(1 qt.) of a sample is usually sufficient. Hazardous wastes usually contain high concentrations of the hazardous components, and only a small aliquot of the sample is used for analysis.

SAMPLING PRECAUTIONS AND PROTECTIVE GEAR

Proper safety precautions must always be observed when sampling hazardous wastes. In all cases, a person collecting a sample must be aware that the waste can be a strong sensitizer and can be corrosive, flammable, explosive, toxic, and capable of releasing extremely poisonous gases.[13] The background information obtained about the waste should be helpful in deciding the extent of sampling safety precautions to be observed and in choosing protective equipment to be used.

For full protection, the person collecting the sample must use a self-contained breathing apparatus, protective clothing, hard hat, neoprene rubber gloves, goggles, and rubber boots.

A self-contained breathing apparatus consists of an air-tight face mask and a supply of air in a pressure tank equipped with a pressure regulator. Protective clothing consists of long-sleeved neoprene rubber coat and pants, or long-sleeved coverall and oil-and-acid proof apron. In hot weather, the coverall-apron combination might be preferred. Table 7 lists the uses and commercial availability of respiratory protective equipment. All equipment except the respirator must be properly washed and cleaned between uses (see Section 5).

TABLE 6. NUMBER OF SAMPLES TO BE COLLECTED

Case No.	Information desired	Waste type	Container type	Number of samples to be collected
1	Average concentration	Liquid	Drum, vacuum truck, and similar containers	1 Collected with Coliwasa
2	Average concentration	Liquid	Pond, pit, lagoon	1 Composite sample of several samples collected at different sampling points or levels
3	Average concentration	Solid (powder or granular)	Bag, drum, bin sack	Same as Case #2
4	Average concentration	Waste pile	--	Same as Case #2
5	Average concentration	Soil	--	1 Composite sample of several samples collected at different sampling areas
6	Concentration range	Liquid	Drum, vacuum truck, storage tank	3 to 10 separate samples, each from a different depth of the liquid
7	Concentration range	Liquid	Ponds, pit, lagoon	3 to 20 separate samples from different sampling points and depths
8	Concentration range	Solid (powder or granular)	Bag, drum, bin	3 to 5 samples from different sampling points
9	Concentration range	Waste pile	--	Same as Case #8
10	Concentration range	Soil	--	3 to 20 separate samples from different sampling areas
11	Average concentration for legal evidence	All types	All containers	3 Identical samples or 1 composite sample divided into 3 identical samples if homogeneous
12	Average concentration	Liquid	Storage tank	Same as Case #2
13	Average concentration	Liquid	Storage tank	Same as Case #6

TABLE 7. RESPIRATORY PROTECTIVE DEVICES RECOMMENDED FOR VARIOUS HAZARDS

Type of hazard	Recommended respiratory device
Oxygen deficiency	Self-contained breathing apparatus, hose mask with blower
Gaseous contaminant immediately dangerous to life	Self-contained breathing apparatus, hose mask with blower, gas mask
Gaseous contaminant not immediately dangerous to life	Air-line respirator, hose mask without blower, chemical-cartridge respirator
Particulate contaminant	Dust, mist, or fume respirator, air-line respirator, abrasive-blasting respirator
Combination of gaseous and particulate contaminants immediately dangerous to life	Self-contained breathing apparatus, hose mask with blower, gas mask with special filter
Combination of gaseous and particulate contaminants not immediately dangerous to life	Air-line respirator, hose mask without blower, chemical-cartridge respirator with special filter

[a]Source: Reference 14.

The self-contained breathing apparatus may not be required in all sampling situations. In some cases, gas masks or chemical cartridge-type respirators with filters will suffice. Table 7 may be used to select the proper protective respiratory device.

• For added protection in sampling, a second person with a radio-telephone and first-aid kit must be present to render any necessary help or call for assistance.

SAMPLING PROCEDURES

The following procedures are recommended for sampling different types of hazardous wastes in various containers.

Sampling a Drum

Drums containing liquid wastes can be under pressure or vacuum. A bulging drum usually indicates that it is under high pressure and should not be sampled until the pressure can be safely relieved. A heavily corroded or rusted drum can readily rupture and spill its contents when disturbed; it should only be sampled with extreme caution. Opening the bung of a drum can produce a spark that might detonate an explosive gas mixture in the drum. This situation is difficult to predict and must be taken into consideration every time a drum is opened. The need for full protective sampling equipment cannot be overemphasized when sampling a drum.

1. Position the drum so that the bung is up (drums with the bung on the end should be positioned upright; drums with bungs on the side should be laid on its side, with the bungs up).

2. Allow the contents of the drum to settle.

3. Slowly loosen the bung with a bung wrench, allowing any gas pressure to release.

4. Remove the bung and collect a sample through the bung hole with a Coliwasa, as directed in Section 4.

5. When there is more than one drum of waste at a site, segregate and sample the drums according to waste types, using a table of random numbers as outlined in Appendix D.

Sampling a Vacuum Truck

Sampling a vacuum truck requires the person collecting the sample to climb onto the truck and walk along a narrow catwalk. In some trucks, it requires climbing access rungs to the tank hatch. These situations present accessability problems to the sample collector, who most usually

wear full protective sampling gear. Preferably, two persons should perform the sampling: One person should do the actual sampling and the other should hand the sampling device, stand ready with the sample container, and help deal with any problems. The sample collector should position himself to collect samples only after the truck driver has opened the tank hatch. The tank is usually under pressure or vacuum. The driver should open the hatch slowly to release pressure or to break the vacuum.

1. Let the truck driver open the tank hatch.

2. Using protective sampling gear, assume a stable stance on the tank catwalk or access rung to the hatch.

3. Collect a sample through the hatch opening with a Coliwasa, as directed in Section 4.

4. If the tank truck is not horizontal, take one additional sample each from the rear and front clean out hatches and combine all three samples in one sample container.

5. When necessary, carefully take sediment sample from the tank through the drain spigot.

Sampling a Barrel, Fiberdrum, Can, Bags, or Sacks Containing Powder or Granular Waste

The proper protective respirator (see Table 7), in addition to the other protective gear, must be worn when sampling dry powdered or granular wastes in these containers. These wastes tend to generate airborne particles when the containers are disturbed. The containers must be opened slowly. The barrels, fiberdrums, and cans must be positioned upright. If possible, sample sacks or bags in the position you find them, since standing them upright might rupture the bags or sacks.

1. Collect a composite sample from the container with a grain sampler or sampler trier, as directed in Section 4.

2. When there is more than one container of waste at a site, segregate and sample the containers according to a table of random numbers, as outlined in Appendix D.

Sampling a Pond

Storage or evaporation ponds for hazardous wastes vary greatly in size from a few to a hundred meters. It is difficult to collect representative samples from the large ponds without incurring huge expense and assuming excessive risks. Any samples desired beyond 3.5 m(11½ ft) from the bank may require the use of a boat, which is very risky, or the use of a crane or a helicopter, which is very expensive. The

information sought must be weighed against the risk and expense of collecting the samples. The pond sampler described in Section 4 can be used to collect samples as far as 3.5 m(11½ ft) from the bank.

1. Collect a composite sample with pond sampler, as directed in Section 4.

Sampling Soil

The techniques of soil sampling are numerous. The procedures outlined below are adopted from ASTM methods.[15] The procedures are consistent with the hazardous waste management objective of collecting soil samples which is usually to determine the amount of hazardous material deposited on a particular area of land or to determine the leaching rate of the material and/or determine the residue level on the soil. Elaborate statistically designed patterns have been designed for sampling soils. If one of these patterns is to be used, a good statistics book may have to be consulted. In the following procedures, soil samples are taken in a grid pattern over the entire site to ensure a uniform coverage.

1. Divide the area into an imaginary grid (see Table 5).

2. Sample each grid and combine the samples into one.

3. To sample up to 8 cm(3 in.) deep, collect samples with a scoop, as directed in Section 4.

4. To sample beyond 8 cm(3 in.) deep, collect samples with a soil auger or Veihmeyer soil sampler, as directed in Section 4.

Sampling a Waste Pile

Waste piles can range from small heaps to a large aggregates of wastes. The wastes are predominantly solid and can be a mixture of powders, granules, and chunks as large as or greater than 2.54 cm(1 in.) average diameter. A number of core samples have to be taken at different angles and composited to obtain a sample that, on analysis, will give average values for the hazardous components in the waste pile.

1. Determine the sampling points (see Table 5).

2. Collect a composite sample with a waste pile sampler according to the directions in Section 4.

Sampling a Storage Tank

The collection of liquid samples in storage tanks is extremely discussed in the ASTM methods. The procedure used here is adopted from one of those methods.[16]

Sampling a storage tank requires a great deal of manual dexterity. Usually it requires climbing to the top of the tank through a narrow vertical or spiral stairway while wearing protective sampling equipment and carry sampling paraphernalia. At least two persons must always perform the sampling: One should collect the actual samples and the other should stand back, usually at the head of the stairway, and observe, ready to assist or call for help. The sample collectors must be accompanied by a representative of the company, who must open the sampling hole, usually on the tank roof.

1. Collect one sample each from the upper, middle, and lower sections of the tank contents with a weighted bottle sampler, as outlined in Section 4.

2. Combine the samples one container and submit it as a composite sample.

SAMPLE HANDLING

After a sample is transferred into the proper sample container, the container must be tightly capped as quickly as possible to prevent the loss of volatile components and to exclude possible oxidation from the air.

The use of a preservative or additive is not recommended. However, if only one or two components of a waste are of interest, and if these components are known to rapidly degrade or deteriorate chemically or biochemically, the sample may be refrigerated at 4 to 6°C.(39.2 to 42.8°F.) or treated with preservatives according to Section 8.

To split or withdraw an aliquot of a sample, considerable mixing, homogenization, or quartering is required to ensure that representative or identical portions are obtained. When transferring a sample aliquot, open the container as briefly as possible.

IDENTIFICATION OF SAMPLE

Each sample must be labeled and sealed properly immediately after collection.

Sample Labels

Sample labels (Figure 11) are necessary to prevent misidentification of samples. Gummed paper labels or tags are adequate. The label must include at least the following information:

Name of collector.

Date and time of collection.

Place of collection.

Collector's sample number, which uniquely identifies the sample.

OFFICIAL SAMPLE LABEL

Collector_____ Collector's Sample No._____

Place of Collection_____

_____

Date Sampled_____ Time Sampled_____

Field Information_____

_____

Figure 11. Example of official sample label.

OFFICIAL SAMPLE SEAL

State of California
Department of Health Services

Public Health Division
Hazardous Materials Laboratory

Collected by_____Collector's Sample No._____
(signature)

Date Collected_____Time Collected_____

Place Collected_____

_____

Figure 12. Example of official sample seal

Sample Seals

Sample seals are used to preserve the integrity of the sample from the time it is collected until it is opened in the laboratory. Gummed paper seals can be used as official sample seals. The paper seal must carry information such as:

Collector's name

Date and time of sampling

Collector's sample number. (This number must be identical with the number on the sample label).

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 12.

FIELD LOG BOOK

All information pertinent to a field survey and/or sampling must be recorded in a log book. This must be a bound book, preferably with consecutively numbered pages that are 21.6 by 27.9 cm(8½ by 11 in.). Entries in the log book must include at least the following:

Purpose of sampling (e.g., surveillance, etc.)

Location of sampling (e.g., hauler, disposal site, etc.) and address

Name and address of field contact

Producer of waste and address

Type of process (if known) producing waste

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

Declared waste components and concentrations

Number and volume of sample taken

Description of sampling point

Date and time of collection

Collector's sample identification number(s)

Sample distribution (e.g., laboratory, hauler, etc.)

References such as maps or photographs of the sampling site

Field observations

Any field measurements made such as pH, flammability, explositivity, etc.

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 situation without reliance on the collector's memory.

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

CHAIN OF CUSTODY RECORD

To establish the documentation necessary to trace sample possession from the time of collection, a chain of custody record must be filled out and accompany every sample. This record becomes especially important when the sample is to be introduced as evidence in a court litigation. An example of a chain of custody record is illustrated in Figure 13.

The record must contain the following minimum information:

Collector's sample number

Signature of collector

Date and time of collection

Place and address of collection

Waste type

Signatures of persons involved in the chain of possession

Inclusive dates of possession

SAMPLE ANALYSIS REQUEST SHEET

The sample analysis request sheet (Figure 14) is intended to accompany the sample on delivery to the laboratory. The field portion of this form must be 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:

Name of person receiving the sample

Laboratory sample number

Date of sample receipt

Sample allocation

Analyses to be performed

SAMPLE DELIVERY TO THE LABORATORY

Preferably, the sample must be delivered in person to the laboratory for analysis as soon as practicable--usually the same day as the sampling. Consult Section 8 when sample preservation is required. The sample must

California Department of Health
Hazardous Materials Laboratory

Collector's Sample No. _____

CHAIN OF CUSTODY RECORD

Hazardous Materials

Location of Sampling: __ Producer __ Hauler __ Disposal Site

__ Other: _____

Company's Name _____ Telephone (___)_____

Address _____
number street city state zip

Collector's Name _____ Telephone (___)_____
signature

Date Sampled _____ Time Sampled _____ hours

Type of Process Producing Waste _____

Waste Type Code _____ Other _____

Field Information _____

_____

_____

Sample Allocation:

1. _____
name of organization
2. _____
name of organization
3. _____
name of organization

Chain of Possession

1.	_____	_____	_____	_____
	signature	title	inclusive	dates
2.	_____	_____	_____	_____
	signature	title	inclusive	dates
3.	_____	_____	_____	_____
	signature	title	inclusive	dates

Figure 13. Example of chain of custody record

PRIORITY_____
(explain)_____

California Department of Health Services
Hazardous Materials Laboratory

HAZARDOUS MATERIALS SAMPLE ANALYSIS REQUEST

PART I: FIELD SECTION

Collector_____ Date Sampled_____ Time_____hours

Location of Sampling_____
name of company, disposal site, etc.

Address_____
number street city state zip

Telephone (___)_____ Company Contact_____

HML NO. (Lab only)	COLLECTOR'S SAMPLE NO.	TYPE OF SAMPLE*	FIELD INFORMATION**

Analysis Requested_____

Special Handling and/or Storage_____

PART II: LABORATORY SECTION

Received by_____ Title_____ Date_____
Sample Allocation: __HML __LBL __LABL __SRL Date_____
Analysis Required_____

*Indicate whether sample is sludge, soil, etc.;**Use back of page for additional information.

Figure 14. Example of hazardous waste sample analysis request sheet

be accompanied by the chain of custody record and by a sample analysis request sheet (Figure 14). The sample must be delivered to the person in the laboratory authorized to receive samples (often referred to as the sample custodian).

SHIPPING OF SAMPLES

When a sample is shipped to the laboratory, it must be packaged in a proper shipping container to avoid leakage and/or breakage. A cardboard box that will provide at least 10 cm(4 in.) of tight packing around the sample container must be used. Acceptable packing materials include sawdust, crumpled newspapers, vermiculite, polyurethane chips, etc. Other samples that require refrigeration must be packed with reusable plastic packs or cans of frozen freezing gels in molded polyurethane boxes with sturdy fiberboard protective case. The boxes must be taped closed with masking tape or fiber plastic tape.

All packages must be accompanied by a sample analysis sheet and chain of custody record. Complete address of the sender and the receiving laboratory must legibly appear on each package. When sent by mail, register the package with return receipt requested. When sent by common carrier, obtain a copy of the bill of lading. Post office receipts and bill of lading copies may be used as part of the chain of custody documentation.[17]

SECTION 7

RECEIPT AND LOGGING OF SAMPLE

Field samples are delivered to the laboratory either personally or through a public carrier. 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.

SAMPLE INSPECTION

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 walls show any bulging or collapsing, the custodian should note that the sample is under pressure or releasing gases, respectively. A sample under pressure should be treated with caution. It can be explosive or release extremely poisonous gases. The custodian should examine whether the sample seal is intact or broken, since broken seal may mean sample tampering and would make analysis results inadmissible in court as evidence. Discrepancies between the information on the sample label and seal and that 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.

ASSIGNMENT OF LABORATORY NUMBER

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.

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 supervisor should then decide what analyses are to be performed. The sample may have to be split with other laboratories to obtain tne necessary information about the sample. The supervisor should decide on the sample allocation and delineate the types of analyses to be performed on each allocation. In his own laboratory, the supervisor should assign the sample analysis to at least one chemist, who is to be responsible for the care and custody of the sample once it is handed to him. 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.

The receiving chemist should record in his laboratory notebook the identifying information about the sample, the date of receipt, and other pertinent information. This record should also include the subsequent analytical data and calculations.

SECTION 8

PRESERVATION AND STORAGE OF SAMPLES

Ideally, hazardous waste samples should be analyzed immediately after collection for maximum reliability of the analytical results. Hazardous wastes are such complex mixtures that it is difficult to exactly predict the physical, biological, and chemical changes that occur in the samples with time. After collection of samples, pH may change significantly in a matter of minutes; sulfides and cyanides may be oxidized or evolve as gases; and hexavalent chromium may slowly be reduced to the trivalent state. Certain cations may be partly lost as a result of adsorption to the walls of the sample containers. Growth of microorganisms may also cause changes to certain constituents of the sample. Volatile compounds may be rapidly lost.

In a number of cases, the above changes may be slowed down or prevented by refrigeration at 4 to 6°C, or by the addition of preservatives. However, these treatments mostly apply to one or two components or properties. Refrigeration may deter the evolution of volatile components and acid gases such as hydrogen sulfides and hydrogen cyanides, but it also introduces the uncertainty that some salts may precipitate at lower temperature. On warming to room temperature for analysis, the precipitates may not redissolve, thus incurring error in determining the actual concentrations of dissolved sample constituents. Addition or preservatives may retard biochemical changes, whereas other additives may convert some constituents to stable hydroxides, salts, or compounds. Unknown in these treatments, however, is the possible conversion of other compounds to other forms (such as the products of nitration, sulfonation, oxidation, etc., of organic components). In subsequent analyses, the results may not reflect the original identity of the components.

Thus, both advantages and disadvantages are associated with the refrigeration and/or addition of preservatives or additives to waste samples. These methods of preservation or stabilization are not recommended for hazardous waste samples unless only one or two components or properties are to be analyzed.

Standard methods books [18,19] have compilations of useful preservatives for various constitutents. Table 8 is excerpted from these lists and shows only the preservation methods that may be used for hazardous wastes.

TABLE 8. METHODS OF PRESERVATION FOR HAZARDOUS WASTES

Waste constituent to be preserved	Preservation method	Storage time
Acidity	Cool to 4° C	24 hr
Alkalinity	Cool to 4° C	24 hr
Ammonia	Add 1 ml conc. H_2SO_4/ℓ	24 hr
Arsenic	Add 6 ml conc. HNO_3/ ℓ	6 months
Chlorine	Cool to 4° C	24 hr
Chromium (VI)	Add 6 ml conc. H_2SO_4/ℓ	24 hr
Cyanides	Add 2.5 ml of 50% NaOH/ℓ ; cool to 4° C	24 hr
Fluoride	Cool to 4° C	7 days
Metals:		
1) dissolved	Filter on site; add 5 ml conc. HNO_3/ℓ	6 months
2) suspended	Filter on site	6 months
3) Total	Add 5 ml conc. HNO_3/ℓ	6 months
Mercury		
1) dissolved	Filter; add 5 ml conc. HNO_3/ℓ	38 days
2) Total	Add 5 ml conc. HNO_3/ℓ	38 days
pH	Determine on site; cool to 4° C	6 hr
Phenolics	Add H_3PO_4 to pH 4 and 1 g. $CuSO_4$/ℓ ; refrigerate at 4° C	24 hr
Residue, volatile	Cool to 4° C	7 days
Selenium	Add 5 ml conc. HNO_3/ℓ	6 months
Specific conductance	Cool to 4° C	24 hr
Sulfide	Add 2 ml of 2N $Zn(AC)_2$/ℓ	24 hr
Sulfide	Cool to 4° C	24 hr
Zinc	Add 4 ml conc. HCl/ℓ	--

[a]Source: References[18,19,and20]

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APPENDICES

APPENDIX A. DEVELOPMENT OF THE COMPOSITE LIQUID WASTE SAMPLER (COLIWASA)

Early in the development of the California waste management program, the needs were recognized for accurate information about waste composition and adequate equipment and procedures for sampling and analysis.

In 1975, the California Department of Health Services engaged in a cooperative study with the University of Southern California (Environmental Engineering Department) under U.S. Environmental Protection Agency's sponsorship to collect and analyze a large number of hazardous waste samples at a number of Class I disposal sites in Los Angeles County. In the preparation of this study, the Department of Health Services personnel designed and constructed a simple tube sampler suitable for use in liquid and sludge wastes. The objective of the sampler design was to obtain samples representative of complex, heterogeneous wastes contained in vacuum trucks and drums. In preliminary testing, the prototype design shown in Figure A-1 appeared to give good representative samples. At this time, the sampling device was named the composite liquid waste sampler, or Coliwasa for short.

Requirements for Hazardous Waste Sampling Procedures and Equipment

Approximately 24 of these devices were constructed for use in the Los Angeles County sampling program. During a 2-week period in 1975, 400 samples of hazardous wastes were taken from vacuum trucks and drums. The wastes represented an extremely wide variety of chemical compositions and physical characteristics. The experience given by this sampling program emphasized the following important requirements of hazardous waste sampling procedures and equipment:

1) Sampling equipment must be of simple design to facilitate easy cleaning or to allow discard if necessary to prevent sample cross contamination. Many wastes, because of their chemical composition and/or physical nature, so fouled sampling equipment that it required discarding or extensive cleaning. Extensive cleaning produces a significant volume of cleaning waste that must be properly disposed. Equipment that has complicated valves, levers, and other fittings would never survive many hazardous wastes.

2) Equipment must be light weight and leak proof. Sampling personnel are required to climb and move about on tank trucks and other dangerous areas while holding sampling equipment. Once the sampler is filled with its

charge of hazardous waste, it must not discharge until properly inside a sample receptacle. Thus, a positive locking mechanism is needed.

3) Several types of sampling equipment must be available, for no one design or material meets all hazardous waste sampling requirements.

4) Sampling requires a minimum of two persons equipped with the proper and complete complement of safety equipment. Even at a well-run waste disposal site using an approved manifest system, surprises occur. A waste sample collector never knows for sure what he will find when a vacuum truck or barrel is opened.

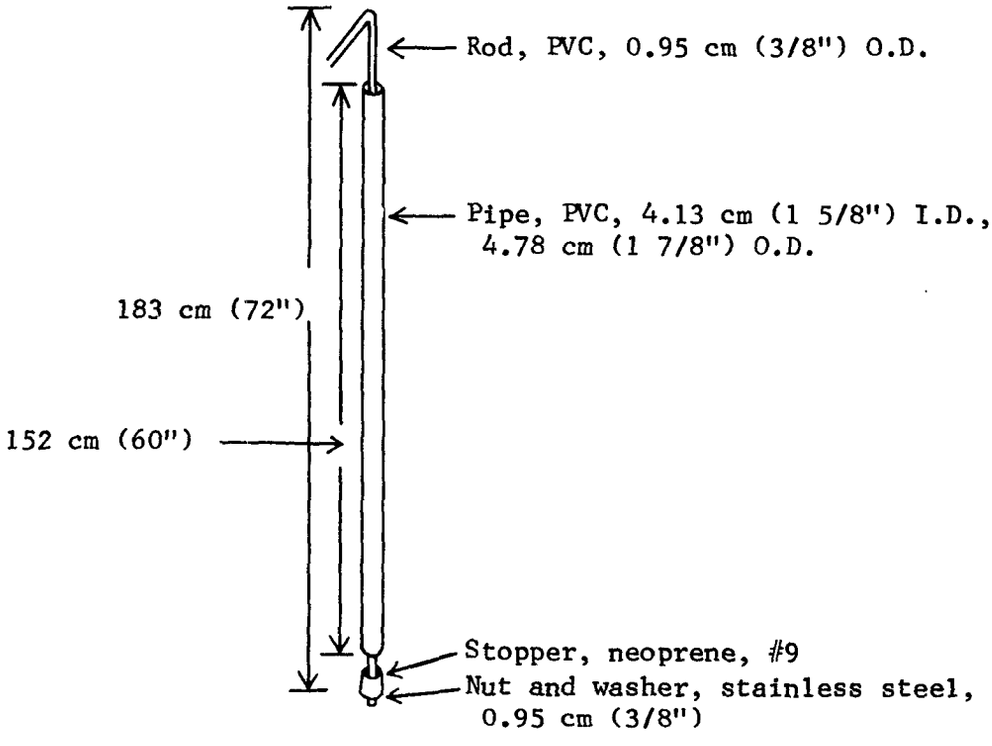

Figure 1. Coliwasa, Model 1.

Sampler Selection

A review of the literature was conducted to investigate the availability of commercial equipment that would better suit the sampling requirements than the Coliwasa. The guidelines used in the selections were commercial availability, cost, simplicity in design, chemical inertness, and adaptability for use in composite sampling of liquid hazardous wastes.

Preliminary tests were performed on a number of candidate liquid samplers. The tests included physical inspections of the sampling mechanisms for ease of operation and applicability. Water was the initial test liquid. The test water was placed in a fabricated tank made out of a

122-cm(4-ft) tall by 15.2-cm(6-in.) I.D. glass cylinder. Each sampler under test was lowered slowly into the tank to determine whether the check valve or closing device or sampling orifice would allow the sample to flow in the sampler. The sampler was then withdrawn and tested for leakage and ease of transfer of the collected sample.

None of the commercially available samplers was found to be satisfactory. The Coliwasa designed by the Department of Health Services appeared to be the most promising.

First Coliwasa Model

The early design of the Coliwasa (Model 1; Figure A-1) consisted of 1.52-m(5-ft.) by 4.13-cm(1 5/8-in.) I.D., opaque PVC pipe as the sampling tube and a neoprene stopper attached to one end of a 0.95-cm(3/8-in.) O.D. PVC rod as the closing mechanism. To collect a sample with this sampler, the stopper is pushed out about 5 cm(2 in.) from the bottom end of the sampling tube. Then the sampler is lowered straight down through the body of liquid waste to be sampled to the bottom of the waste container. The liquid in the tube is trapped by plugging the bottom of the tube with the stopper by pulling up the stopper rod with one hand and holding the tube with the other hand.

This early design of the Coliwasa, albeit functional, was deficient in a number of aspects. First, it was difficult to put the sampler in the close position. The stopper did not easily line up with the bottom opening of the sampling tube. Several manipulations of the stopper rod were usually required to effect closure. This difficulty tended to disturb the bottom layer of the waste being sampled and undoubtedly contributed to the collection of nonrepresentative samples.

Second, the sampler was not equipped with a mechanism that positively and independently locked it closed. Closure was maintained by using one hand to hold the sampling tube and the other hand to maintain a constant upward pressure on the upper end of the stopper rod to keep the stopper tightly seated against the bottom opening of the sampler. In some sampling instances, this method of closure was not always practical. When sampling waste containers as deep as the length of the sampler, the operator could not withdraw the sampler without freeing the hand that maintains the closing pressure on the stopper rod. Thus, the snug contact between the neoprene stopper and the inner opening of the sampling tube was the only force that locked the sampler closed. The weight of the sample contained in the sampling tube has in some cases pushed out the stopper, resulting in lost samples and exposure of the sample collector to unnecessary hazards.

Third, samples contained in the sampler were difficult to transfer into sample containers at regulated rates, and caused some samples to be lost from splashings.

Attempts were made to improve the first model of the Coliwasa. These efforts led to fabrication of the other models shown in Figures A-2 through A-5, and finally to the recommended version as shown in Figure 1 of the text.

Models 2 and 3

The improvement in the second model of the Coliwasa (Figure A-2) consisted of making diametrical slits, 5 cm(2 in.) deep by 2 cm(0.79 in.) wide, and indentations 90° from the slits at the top of the sampler tube. The slits accommodate the T-handle of the stopper rod in the open position, which allows the stopper to extend down about 5 cm(2 in.) below the bottom of the sampler. The indentations serve as support for the T-handle when the sampler is placed in the close position. When this improved Coliwasa was tested the neoprene stopper still did not readily line up with the bottom opening of the sampling tube. Several twisting manipulations of the stopper rod were required to bring the sampler into the close position. This problem was remedied by installing three stainless steel guide wires (18 gauge) on the stopper, with the upper wire ends secured to the stopper rod, as shown in Figure A-3. This version (Model 3) of the sampler was again tested. The sampler was found functional and relatively easy to operate. It can be disassembled and reassembled for cleaning in about 2 minutes. It can be built for less than $10.00. The closing tension on the stopper of this sampler, however, is not easily adjusted while sampling. This drawback might incur some sample loss.

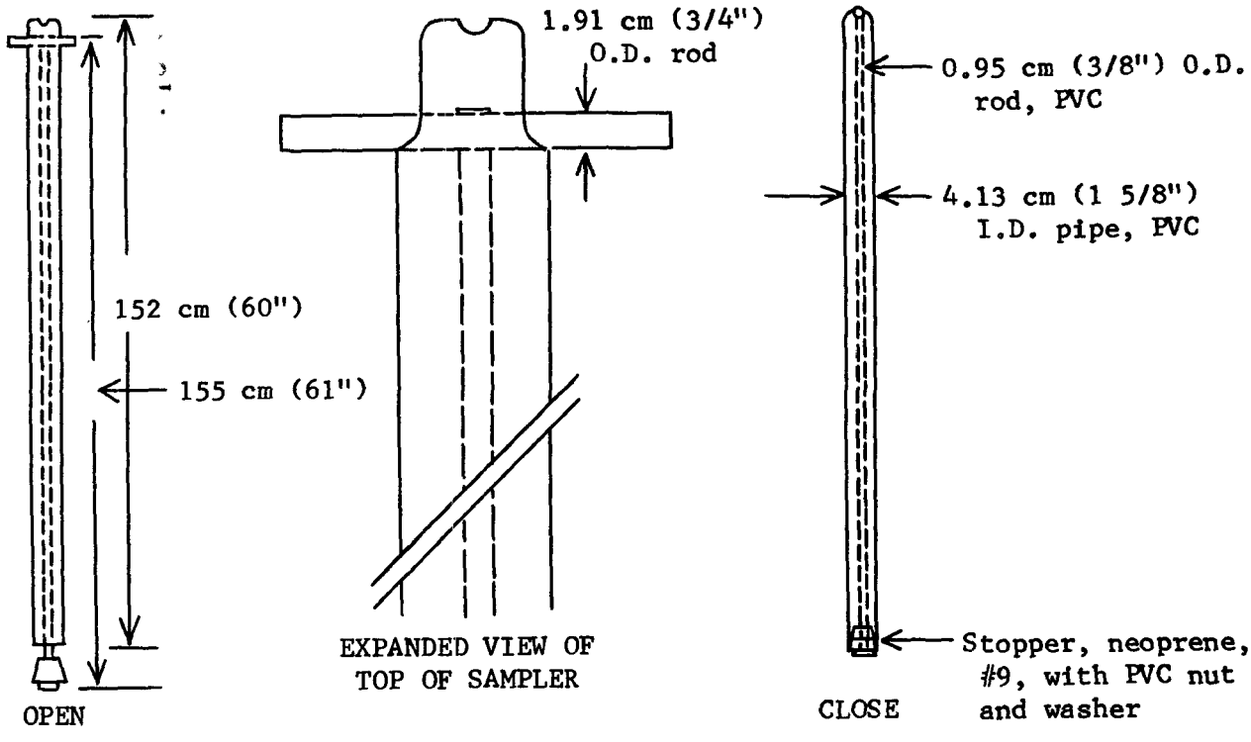

Figure A-2. Coliwasa, Model 2.

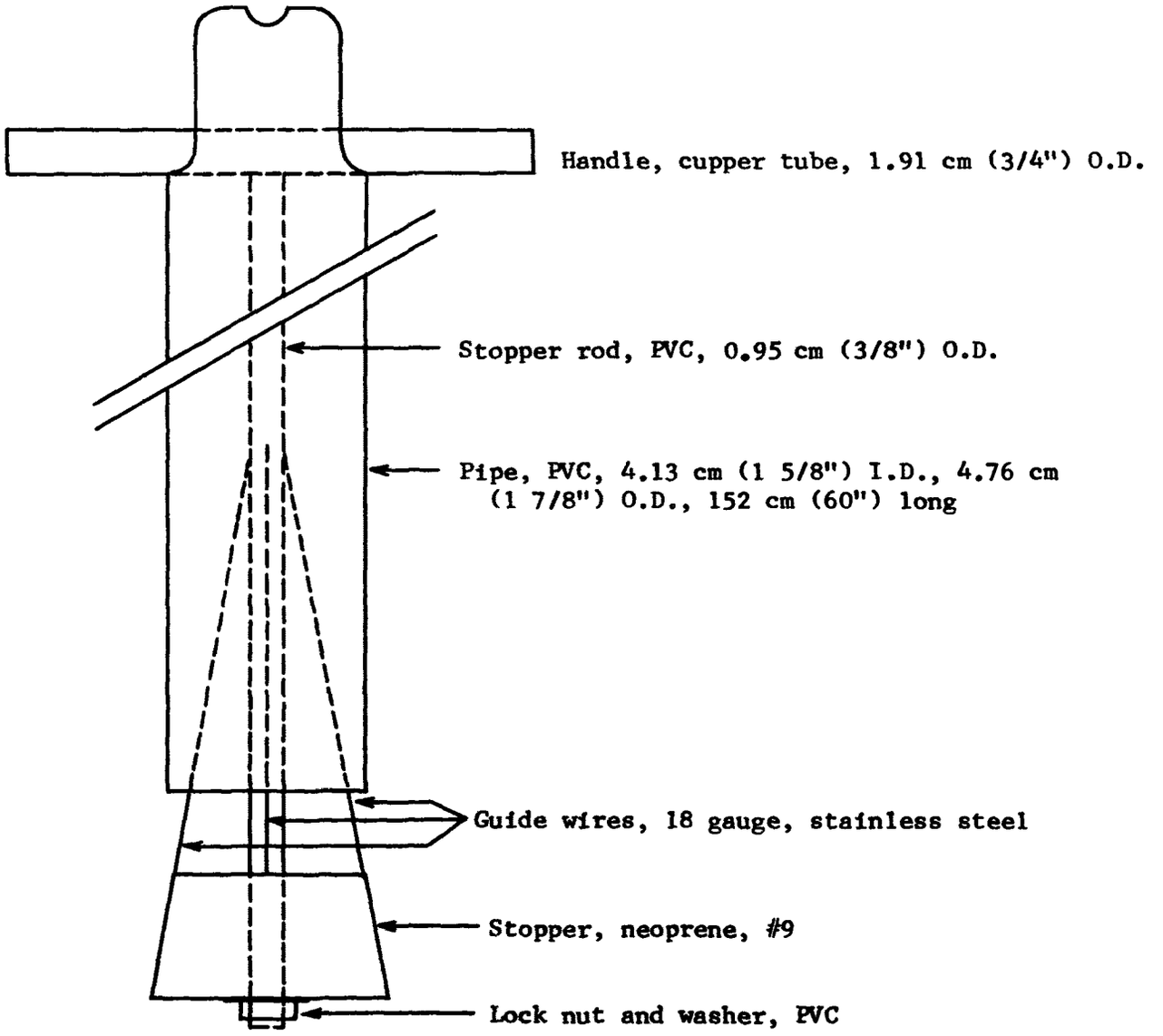

Figure A-3. Coliwasa, Model 3.

Model 4

Further investigation into improving the design of the Coliwasa resulted in Model 4(Figure A-4). In this version, the locking mechanism of the sampler consisted of a threaded PVC plug that rides on a short threaded 0.95-cm(3/8-in.) O.D. metal rod. The metal rod is coupled with the PVC stopper rod. To sample, the plug is screwed out about 5 cm and then the stopper rod is pushed downward to open the sampler. The sampler is lowered slowly into the liquid. Upon reaching the bottom of the container, the stopper rod is pulled up to close the sampler. The PVC plug is screwed in until tight to secure the stopper in the close position. This design of the Coliwasa is simple, functional, and provides the person collecting the sample with control over the tightness of the stopper against the bottom of the sampler. It is, likewise, easily disassembled and reassembled for cleaning. This sampler, however, is slow to operate, the PVC plug does not screw in and out fast enough. This drawback tends to expose the sample collector to the liquid waste during sampling longer than is perhaps necessary.

Model 5

Another model of the Coliwasa was fabricated using a closing principle similar to a float valve (Figure A-5). This sampler was fabricated from a 1.52-m(5-ft) by 5.1-cm(2-in.) I.D. plastic pipe. At the bottom end is a plastic reducer fitting (5.1-cm(2-in.) to 3.18-cm(1.5-in.) I.D.). A manually operated neoprene rubber plug attached to a rod is used as the closing device. When sampling, the rubber plug is raised about 5 cm(2-in.) above its seat, and the sampler is slowly lowered into the liquid. On reaching the bottom of the container, the sampler is closed by slowly lowering the plug back to its seat. The sampler is withdrawn and the sample is discharged into a sample container. Tests performed on this sampler showed no leakage of collected samples. This sampler was also found to be the easiest to disassemble and reassemble for cleaning. However, the annular clearance between the outside diameter of the stopper and the inside diameter of the sampling tube was too narrow. The sampler tended to stir the liquid mixture on filling, which could incur the collection of nonrepresentative sample. In addition, the sampler tended to exclude large particles in the wastes. Increasing the tube/stopper annular clearance did not seem practical because it conversely reduced the opening of the reducer fitting of the sampling tube.

Final Design

A much improved and recommended model of the Coliwasa is shown in Figure 1 of the text. This model features three main improvements over the previous models. The first improvement consists of the use of a positive, quick engaging closing and locking mechanism. This mechanism consists of a short-length, channeled aluminum bar that is attached to the sampler's stopper rod by an adjustable swivel. The aluminum bar serves both as a T-handle and lock for the sampler's closure system. When the sampler is in the open position, the handle is placed in the T-position and pushed down agains the locking block. This manipulation pushes out the

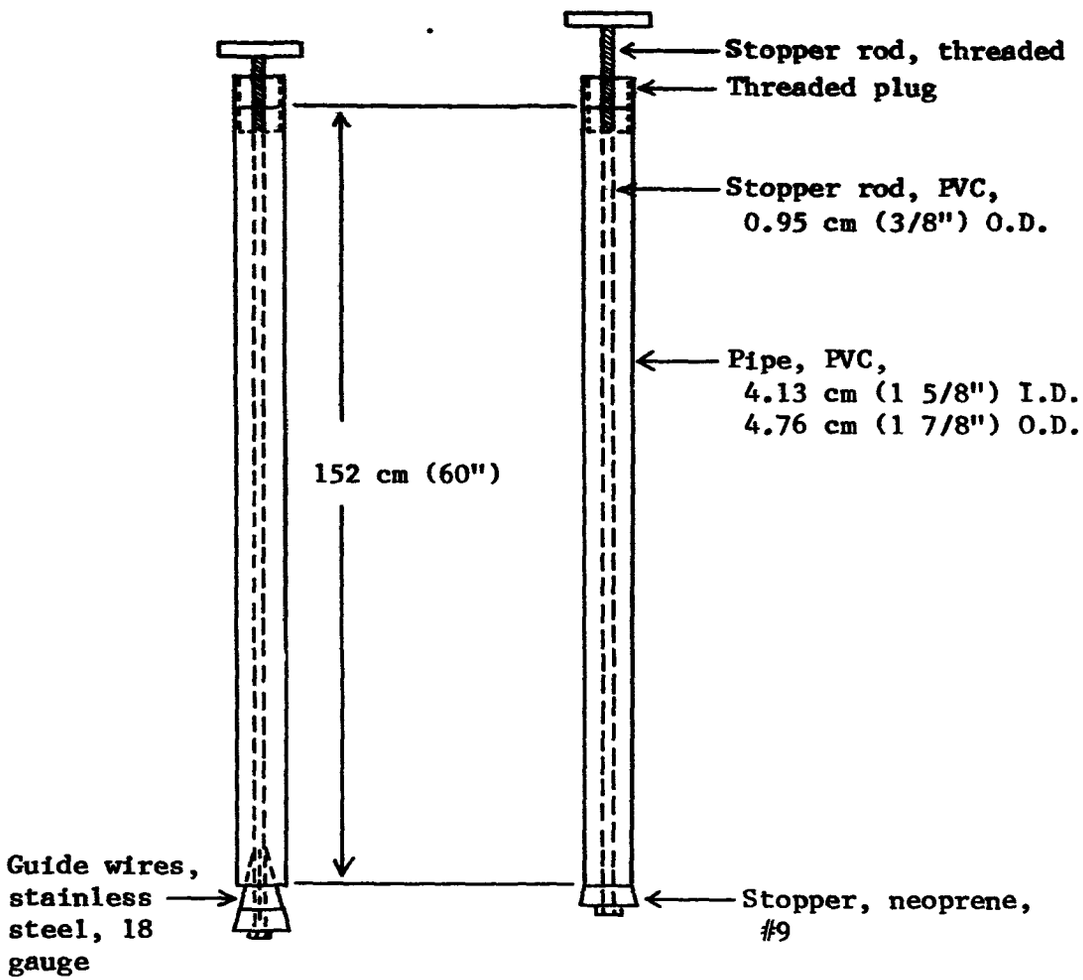

Figure A-4. Coliwasa, Model 4.

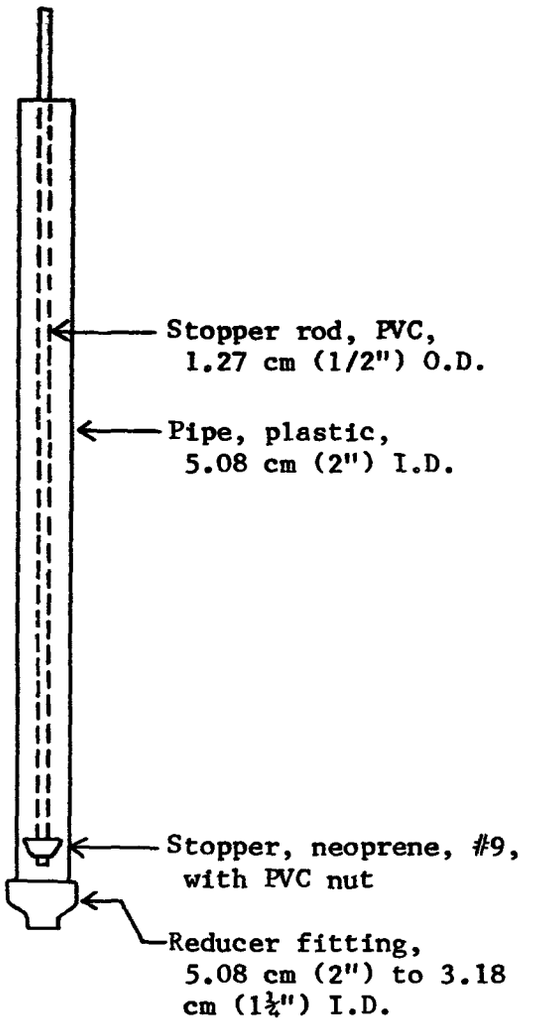

Figure A-5. Coliwasa, Model 5.

neoprene stopper and opens the sampling tube. In the close position, the handle is rotated until one leg of the T is squarely perpendicular against the locking block. This tightly seats the neoprene stopper against the bottom opening of the sampling tube and positively locks the sampler in the close position. The closure tension can be adjusted by shortening or lengthening the stopper rod by slightly screwing it in or out of the T handle swivel. In discharging a collected sample, the T handle is slowly brought into the T-position. This facilitates the opening of the sampler at a controllable rate and permits the transfer of the sample into a sample container at a regulated rate, thus minimizing splashing or loss of sample.

The second improvement made is the use of a sharply tapered neoprene stopper. The sharp taper of the stopper eliminates the use of guide wires and facilitates the proper seating of the stopper against the opening of the sampling tube on closure. This stopper can be fabricated to specfications by plastic products manufacturers at an extremely high price, or it can be made by simply grinding down the inexpensive and commercially available neoprene stopper to the desired taper with a shop grinder (Note 1 in Appendix B).

The third improvement is the use of translucent PVC and glass pipes as the sampling tubes. These tubes permit the observation of the phases of the liquid waste sample collected in the sampler. The glass sampling tube is usually used with a Teflon stopper rod. Each tube is used for different purposes, as described in Section 4 of the text.

The improved model of the Coliwasa was tested in the field and in the laboratory and found to be the most practical and capable of collecting representative samples of multiphase liquid wastes samples.

Laboratory Tests

In the laboratory, the testing was conducted using test liquid mixtures in a 122-cm (4-ft) tall by 15.2-cm(6-in.) I.D. glass cylindrical tank. The glass tank was ideal for the tests because it permitted observation and measurement of the relative heights of the liquid phases.

A two-phase liquid mixture consisting of about 13.9 liters of water and 3.29 liters of waste oil was sampled with the Coliwasa. The sample was emptied into a 1000-ml (1.056 qt) graduated cylinder. The relative volumes of the liquids were determined and given in Table A-1.

The results indicate that the Coliwasa is capable of obtaining a representative sample of a two-phase liquid mixture.

TABLE A-1.

Relative Volumes of Liquids in the Two-Phase Mixture

Item	Oil	Water
% by height of phases in tank	19	81
% by volume collected	22	78

A three-phase mixture was sampled next. The mixture was prepared by combining waste oil, water, and trichloroethylene (TCE) in the test tank. The TCE extracted some of the waste oil and foamy emulsions formed at the oil/water and the water/TCE interfaces. However, three distinct phases were still obtained. Just like the previous experiment, the starting heights of the liquid phases for each trial were measured. The mixture was sampled with the Coliwasa. The samples were each discharged into 1000-ml (1.056 qt) graduated cylinders and the relative volumes of the liquid phases were determined (Table A-2).

TABLE A-2.

Relative Volumes of Liquids in the Three-Phase Mixture

Item	Oil	Aqueous	TCE
Trial I:			
% by height of phases in tank	7.9	77.4	14.7
% by volume collected	9.7	79.6	10.8
Trial II:			
% by height of phases in tank	9.3	75.0	15.0
% by volume collected	10.2	79.0	10.7
Average:			
% by height of phases in tank	8.8	76.0	15.0
% by volume collected	9.8	79.0	11.0

The results indicate that the Coliwasa is capable of collecting a representative sample of a three-phase mixture within 5% accuracy. The greatest nonrepresentative error, as anticipated, occured at the bottom phase because the sampler's rubber stopper prevents sampling of the last 2.54 cm(1 in.) to the bottom of the container. This error decreases as the bottom phase increases in volume as compared to the upper phases. With less viscous and completely immiscible test liquids, the representativeness of the sample collected approaches unity.

Field Tests

The field tests consisted of sampling liquid wastes in drums and in vacuum trucks. Drums of unknown liquid wastes are sampled at a hazardous waste (Class I) disposal site in California. The sampler, which has a 4.8-cm (1 7/8-in.) O.D., easily cleared through the drum's bung holes.

Sampling was relatively fast. From the time a drum was opened, a sample was collected and transferred into a container in less than 5 minutes. While a sample was in the sampler, no leakage was detected, indicating a positive seal by the sampler's closing mechanism. On the transfer of sample to a container, no splashings were observed, showing that the sampler's content can be discharged at a regulated rate.

A drum containing a two-phase liquid waste mixture was also sampled. Replicate samples were obtained, and each was placed in separate containers. The ratios of the liquid phases in each of the samples were determined and found to be approximately the same, indicating that reproducible samples can be collected with the sampler.

Incoming vacuum trucks carrying liquid wastes to the disposal site were sampled next with the Coliwasa. Again, the sampler was found to be functional and very easy to use. Collection of samples was very fast, minimizing the exposure of the sample collector to hazardous fumes and other emissions from the wastes. Only one vacuum truck with a narrow hatch opening and a total depth of about 163 cm(5.3 ft) was not successfully sampled. The sampling tube of the Coliwasa is only 152 cm(5 ft) long. A longer sampling tube (i.e.,183 cm(6 ft) long) could have remedied the problem.

APPENDIX B. PARTS FOR CONSTRUCTING THE COLIWASA

Item	Supplier	Approximate Cost[a]
Sample tube, PVC plastic, translucent, 4.13 cm(1 5/8 in.) I.D. X 1.52 m(5 ft) long X 0.4 cm(5/32 in.)	Plastic supply houses	$ 4.00 each
Sample tube, glass borosilicate, 4.13 cm(1 5/8 in.) I.D. X 1.52 m (5 ft) long, Code 72-1602.	Corning Glass Works, Corning, N.Y.	$18.00 each
Stopper, rubber, neoprene, #9, modified as described in footnote.[b]	Laboratory supply	$ 6.00/0.45 kg(1b)
Stopper rod, PVC, 0.95 cm(3/8 in.) O.D. X 1.67 m(5½ ft) long.	Plastic supply houses	$ 5.00/6.1 m (20 ft)
Stopper rod, Teflon, 0.95 cm(3/8 in.) O.D. X 1.67 m(5½ ft) long.	Plastic supply houses	$30.00/3.05 m (10 ft)
Locking block without sleeve, PVC, 3.8 cm(1½ in.) O.D. X 10.2 cm(4 in.) long with 1.11-cm(7/16 in.) hole drilled through center.	Fabricate. Rods available at plastic supply houses. Can be bought in 30.48 cm(1 ft)length	
Sleeve, PVC, 4.13 cm(1 5/8 in.) I.D. X 6.35 (2½ in.) long.	Fabricate from stock of 4.13 cm(1 5/8 in.) I.D. PVC pipe. Available at plastic supply houses	$ .80/30.48 cm(ft)
T-handle, aluminum, 18 cm(7 in.)long X 2.86 cm(1 1/8 in.) wide with 1.27 cm(½ in.) wide channel.	Fabricate. Aluminum bar stock available at hardware stores.	$3.00/1.83 m(6 ft)
Swivel, aluminum bar, 1.27 cm(½ in.) square X 3.8 cm(1½ in.)long with 3/8 National Coarse (NC) inside thread to attach stopper rod.	Fabricate. Aluminum bar stock available at hardware stores.	$ 3.00/1.83 m(6 ft)
Nut, PVC, 3/8 in. NC thread	Plastic supply houses	$ .03 each
Washer, PVC, 3/8 in.	Plastic supply houses	$ .03 each
Nut, SS, 3/8 in., NC	Hardware stores	$ .10 each
Washer, SS, 3/8 in.	Hardware stores	$ .10 each
Bolt, 3.12 cm(1 ¼ in.)long X 3/16 in.	Hardware stores	$ .10 each
Nut, 3/16 in., NC	Hardware stores	$ .03 each
Washer, lock 3/16 in.	Hardware stores	$ .03 each

[a] 1977 prices

[b] Shape the stopper into a cone as follows: Bore a 0.95-cm(3/8-in.) diameter center hole through the stopper. Insert a short piece of 0.95-cm(3/8 in.) 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(3/16 in.) of the top (larger diameter) surface to the edge of the 0.95-cm(3/8-in.) hole on the bottom surface.

APPENDIX C. CHECKLIST OF ITEMS REQUIRED IN THE FIELD SAMPLING OF HAZARDOUS WASTES.

Quantity	Item	Use	Supplier	Approximate Cost
1	Coliwasa, plastic type (Section 4)	To sample liquid wastes, except ketones, nitrobenzene, dimethylforamide, tetrahydrofuran and pesticides	Fabricate; Parts can be purchased from hardware stores (see Section 4)	$ 16.00
1	Coliwasa, glass type (Section 4)	To sample liquid waste with pesticides, and other wastes that cannot be sampled with plastic Coliwasa except strong alkali and hydrofluoric acid solution	Fabricate; Glass tube available from Corning Glass Co. Corning, N.Y.14830 (see Section 4)	$ 25.00
1	Soil sampler, auger (Section 4)	To sample contaminated soil, dried ponds, etc.	Weyco Distributor 1417 Heskett Way Sacramento, Calif. 95825	$ 70.00
1	Grain sampler (Section 4)	To sample powdered or granular wastes	Laboratory supply houses	$ 50.00
1	Scoop, stainless steel blade (Section 4)	To sample top soil or shallow layers of solid wastes	Cole-Parmer Instruments Chicago, Ill.	$ 25.00

APPENDIX C (continued).

Quantity	Item	Use	Supplier	Approximate Cost
1	Veihmeyer soil sampler (Section 4)	To collect soil core samples	Hansen Machine, 334 N. 125h St., Sacramento,Calif. 95815	$ 200.00
1	Pond sampler (Section 4)	To sample ponds, pits, etc.	Fabricate (see Section 4).Clamps available at Cole-Parmer Instrument 3060 Gibraltar Ave. Costa Mesa,Calif. 92626	$ 9.00
			Telescoping handle available at swimming pool supply houses	$ 16.24
1	Trier, single slot (Section 4)	To sample granular and powdered material in piles, sacks, fiberdrums, etc.	Curtin-Matheson Scientific 470 Valley Drive P.O.Box 386 Brisbane,Calif. 94005	$ 25.00
1	Waste pile sampler (Section 4)	To sample waste piles	Fabricate. PVC pipe available at hardware stores (see Section 4)	$ 3.00
6	1000-,2000-ml(1-qt,2-qt) linear polyethylene	To contain solid and liquid samples except pesticides and chlorinated hydrocarbons	Laboratory supply houses	$ 11.00/ pkg.6
1	Coverall, long-sleeved, cotton	Protective garment	Clothing stores	$ 14.00
1	Suit, neoprene rubber, long-sleeved	Protective garment	MSA,Catalog #33496	$ 210.00
1 pair	Gloves, neoprene rubber	Protective garment	Laboratory supply houses	$ 4.20

APPENDIX C (continued).

Quantity	Item	Use	Supplier	Approximate Cost
1	Self-contained breathing apparatus	For use in atmospheres deficient in oxygen or otherwise immediately dangerous to life.	MSA,Catalog #461704, Model 401 or equivalent	$580.00
1	Respirator, chemical cartridge type	For use in atmospheres not immediately dangerous to life	Comfo 11 Respirator, MSA,Catalog #460968 or equivalent	$ 9.00
4	Cartridges for respirator	For use in atmospheres not immediately dangerous to life	GMC Cartridge,MSA Cat.#459317 & GMD Cartridge, MSA Cat.#459318 or equivalent	$ 5.00
1 pair	Goggles	Eye protection	MSA,Cat.#79179 or equivalent	$ 5.00
1	Portable eyewash	For emergency eyewash	Laboratory supply houses	$ 4.00
1	Fire extinquisher	Fire suppression	Scientific Products S1365-1 or equivalent	$ 60.00
1	Hard hat	Head protection	MSA, Cat.#454740 or equivalent	$ 5.00
1	Gas mask	For use in contaminated atmospheres immediately dangerous to life	MSA, Cat.#448983 or equivalent	$ 70.00
1	18.9-liter (5-gal) water in cubitainer or equivalent with spigot	For miscellaneous washing purposes	Laboratory supply houses	$ 5.50
6	Teflon liners for Bakelite caps	To provide inert cap liners	Scientific Specialties, P.O.Box 352 Randallstown, Md. 21133 or other suppliers	$ 9.00
12 each	Sample labels, seals, sample analysis request sheets, chain of custody records	To document sample	Design using information from Section 6	

APPENDIX C (continued).

Quantity	Item	Use	Supplier	Approximate Cost
1	Field log book (Section 6)	To keep sample records	Office supply stores	$ 2.00
1	Weighted bottom sampler (Section 4)	To sample storage tanks or similar containers	Fabricate (see Section 4 and Figure 9)	$ 25.00
1	Disposable towels or rags	To clean sampling equipment	Terry towels or equivalent. Available at chemical supply houses	$ 4.00/ pkg.
6	Large polyethylene bags	To store waste papers, rags, etc.	Plastic supply houses	$ 11.00/ pkg/100
12	Polyethylene bags	To store sample containers	Plastic supply houses	$ 4.00/ pkg/100
4	Waterproof pens	To complete records and labels	Stationery stores	$ 3.00
1	Technical grade trichloroethylene	To clean samplers	Chemical supply stores	$ 22.00/ gal.
1	Apron, oil and acid proof	Protective garment	McMaster-Carr Co. P.O.Box 4355 Chicago, Ill.	$ 9.00
1	Face mask	Protective garment	MSA 400 Penn Center Blvd. Pittsburg, Pa. 15235	$ 4.00
1	18.9 liter (5-gal) can	To store used cleaning solvent	Hardware stores	$ 5.00

APPENDIX D. RANDOM SAMPLING

Random Numbers

03	47	43	73	86	36	96	47	36	61	46	98	63	71	62
97	74	24	67	62	42	81	14	57	20	42	53	32	37	32
16	76	62	27	66	56	50	26	71	07	32	90	79	78	53
12	56	85	99	26	96	96	68	27	31	05	03	72	93	15
55	59	56	35	64	38	54	82	46	22	31	62	43	09	90
16	22	77	94	39	49	54	43	54	82	17	37	93	23	78
84	42	17	53	31	57	24	55	06	88	77	04	74	47	67
63	01	63	78	59	16	95	55	67	19	98	10	50	71	75
33	21	12	34	29	78	64	56	07	82	52	42	07	44	38
57	60	86	32	44	09	47	27	96	54	49	17	46	09	62
18	18	07	92	46	44	17	16	58	09	79	83	86	19	62
26	62	38	97	75	84	16	07	44	99	83	11	46	32	24
23	42	40	64	74	82	97	77	77	81	07	45	32	14	08
52	36	28	19	95	50	92	26	11	97	00	56	76	31	38
37	85	94	35	12	83	39	50	08	30	42	34	07	96	88
70	29	17	12	13	40	33	20	38	26	13	89	51	03	74
56	62	18	37	35	96	83	50	87	75	97	12	25	93	47
99	49	57	22	77	88	42	95	45	72	16	64	36	16	00
16	08	15	04	72	33	27	14	34	09	45	59	34	68	49
31	16	93	32	43	50	27	89	87	19	20	15	37	00	49

HOW TO USE THE TABLE OF RANDOM NUMBERS:

1. Based on available information, segregate the containers (i.e., drums, sacks, etc.) according to waste types.
2. Number the containers containing the same waste types consecutively, starting from 01.
3. Decide on how many samples you wish to take. This number is usually determined by the objective of the sampling. For regular surveillance sampling, the collection of one or two samples is usually adequate. In this case, random sampling is not necessary. But for regulatory or research purposes, more samples (such as one sample for every group of five containers) taken at random will generate more statistically valid data. Hence if there were 20 drums containing the same type of waste, 5 drums have to be sampled.
4. Using the set of random numbers above, choose any number as a starting point.
5. From this number, go down the column, then to the next column to the right, or go in any predetermined direction until you have selected five numbers between 01 and 20, with no repetitions. Larger numbers are ineligible.

   Example: If you were to choose 19 as the starting point on column four, the next eligible numbers as you go down this column are 12 and 04. So far you have chosen only three

eligible numbers. Proceed to the next column to the right. Going down and starting from the top of this column, the next eligible numbers are 12 and 13. But 12 is already chosen. Proceeding to the sixth column, the next eligible number is 16. Your five random numbers, therefore, are 19, 12, 04, 13 and 16. Thus the drums with corresponding numbers have to be sampled.

APPENDIX E. SYSTEMATIC ERRORS USING THE COLIWASA

Certain systematic errors may occur in the determination of relative phase composition of waste when using the Coliwasa. This error, in which certain phases are disproportionately represented, results from the use of a straight-sided sample tube to sample a container (tank truck) with a circular cross section. On the basis of a two-phase system, error is at a minimum when the phase interface is at the tank center and at a maximum when the interface is near the bottom or top of the tank. These errors do not occur when sampling a drum or other container when sampling is done down the axis of the container (cylinder).

Errors in relative phase composition encountered in sampling the typical cylindrical vacuum truck may be estimated using Table E-1. Numbers given in the table are representative values calculated from the equations given below, which relate the geometry of the sample tube to the geometry of the tank truck.

$$\% A(\text{tank}) = \frac{(\theta - \text{Sin } \theta)}{2\pi}$$

$$\% A(\text{sample}) = \frac{1 - \text{Cos } \frac{1}{2}\theta}{2}$$

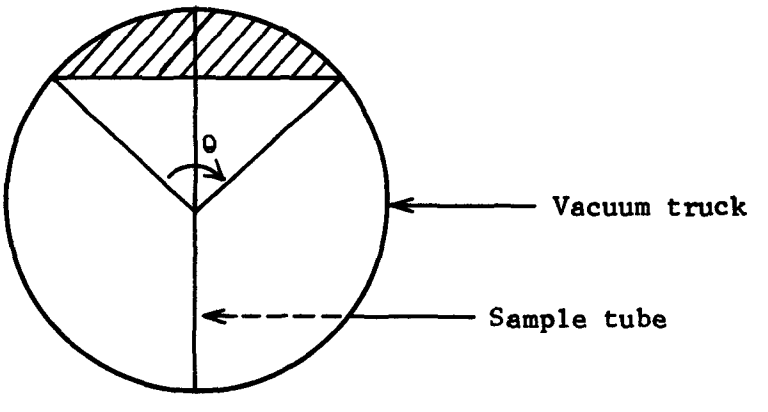

TABLE E-1. SAMPLE VOLUME CORRECTION FACTORS WHEN SAMPLING CYLINDRICAL TANKS WITH COLIWASA

% A in sample	% A in tank	Correction (%)
10	5.20	+ 4.80
20	14.2	+ 5.8
30	25.2	+ 4.8
40	37.4	+ 2.6
50	50	0
60	62.6	- 2.6
70	74.8	- 4.8
80	85.8	- 5.8
90	94.8	- 4.8
100	100	0

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16. ABSTRACT

The goal of this project was to develop simple but effective sampling equipment and procedures for collecting, handling, storing, and recording samples of hazardous wastes. The report describes a variety of sampling devices designed to meet the nee of those who regulate and manage hazardous wastes. Particular emphasis is given to the development of a composite liquid waste sampler, the Coliwasa. This simple devi is designed for use on liquid and semi-liquid wastes in a variety of containers, tan and ponds. Devices for sampling solids and soils are also described.

In addition to the sampling devices, the report describes procedures for develc ment of a sampling plan, sample handling, safety precautions, proper recordkeeping and chain of custody, and sample containment, preservation, and transport. Also discussed are certain limitations and potential sources of error that exist in the sampling equipment and the procedures. The statistics of sampling are covered briefly, and additional references in this area are given.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Grou
Samplers Lagoons (ponds)--waste disposal Hazardous materials	Representative sampling Composite sampling Sampling plans Sampling procedures Hazardous waste Composite liquid waste sampler	68C

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APPENDIX II

METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

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METHODS FOR CHEMICAL ANALYSIS OF WATER AND WASTES

March 1979

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

DISCLAIMER

The mention of trade names or commercial products in this manual is for illustration purposes, and does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

FOREWORD

The accomplishment of our objective in protecting the environment requires a reliable assessment of the present condition and a determination of the effectiveness of corrective measures. Decisions which must be made on the need for pollution abatement and the most efficient means of achieving environmental quality depend upon the availability of sound data. Test procedures for measurement of the presence and concentration of substances hazardous to human health as well as an evaluation of the quality of the environment are essential to satisfactory decision-making.

This manual of chemical methods was prepared by the staff of the Environmental Monitoring and Support Laboratory of the Environmental Research Laboratory, Cincinnati to provide procedures for monitoring water supplies, waste discharges, and the quality of ambient waters. These test methods have been carefully selected to meet the needs of Federal Legislation and to provide guidance to laboratories engaged in protecting human health and the aquatic environment. The contributions and counsel of scientists in other EPA laboratories are gratefully acknowledged.

Test procedures contained herein, that are approved for water and waste monitoring under the Safe Drinking Water Act (SDWA) and the National Pollutant Discharge Elimination System (NPDES), of PL 92–500 are so indicated at the bottom of each title page. These approved methods are also recommended for ambient monitoring needs of Section 106 and 208 of PL 92–500. Methods without this stated approval are presented for information only. Correspondence on these methods is invited.

Dwight G. Ballinger
Director, Environmental Monitoring and
Support Laboratory, Cincinnati, Ohio 45268

ABSTRACT

This manual provides test procedures approved for the monitoring of water supplies, waste discharges, and ambient waters, under the Safe Drinking Water Act, the National Pollutant Discharge Elimination System, and Ambient Monitoring Requirements of Section 106 and 208 of Public Law 92-500. The test methods have been selected to meet the needs of federal legislation and to provide guidance to laboratories engaged in the protection of human health and the aquatic environment.

CONTENTS

200 Metals

300 Inorganic, Non-metallics

INTRODUCTION

This third edition of "Methods for Chemical Analysis of Water and Wastes" contains the chemical analytical procedures used in U.S. Environmental Protection Agency (EPA) laboratories for the examination of ground and surface waters, domestic and industrial waste effluents, and treatment process samples. Except where noted under "Scope and Application", the methods are applicable to both water and wastewaters, and both fresh and saline water samples. The manual provides test procedures for the measurement of physical, inorganic, and selected organic constituents and parameters. Methods for pesticides, industrial organic waste materials, and sludges are given in other publications of the Agency. The methods were chosen through the combined efforts of the EPA Regional Quality Assurance Coordinators, the staff of the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, and other senior chemists in both federal and state laboratories. Method selection was based on the following criteria:

(1) The method should measure the desired property or constituent with precision, accuracy, and specificity sufficient to meet the data needs of EPA, in the presence of the interfering materials encountered in water and waste samples.
(2) The procedure should utilize the equipment and skills available in modern water pollution control laboratories.
(3) The selected method is in use in many laboratories or has been sufficiently tested to establish its validity.
(4) The method should be rapid enough to permit routine use for the examination of a large number of samples.

Instrumental methods have been selected in preference to manual procedures because of the improved speed, accuracy, and precision. In keeping with this policy, procedures for the Technicon AutoAnalyzer have been included for laboratories having this equipment available. Other continuous flow automated systems using these identical procedures are acceptable.

Intralaboratory and interlaboratory precision and accuracy statements are provided where such data are available. These interlaboratory statements are derived from interlaboratory studies conducted by the Quality Assurance Branch, Environmental Monitoring and Support Laboratory; the American Society for Testing Materials; or the Analytical Reference Service of the US Public Health Service, DHEW. These methods may be used for measuring both total and dissolved constituents of the sample. When the dissolved concentration is to be determined, the sample is filtered through a 0.45-micron membrane filter and the filtrate analyzed by the procedure specified. The sample should be filtered as soon as possible after it is collected, preferably in the field. Where field filtration is not practical, the sample should be filtered as soon as it is received in the laboratory.

Many water and waste samples are unstable. In situations where the interval between sample collection and analysis is long enough to produce changes in either the concentration or the physical state of the constituent to be measured, the preservation practices in Table I are recommended.

This manual is a basic reference for monitoring water and wastes in compliance with the requirements of the Federal Water Pollution Control Act Amendments of 1972. Although other test procedures may be used, as provided in the Federal Register issue of October 16, 1973 (38FR 28758) and in subsequent amendments, the methods described in this manual will be used by the Environmental Protection Agency in determining compliance with applicable water and effluent standards established by the Agency.

Although a sincere effort has been made to select methods that are applicable to the widest range of sample types, significant interferences may be encountered in certain isolated samples. In these situations, the analyst will be providing a valuable service to EPA by defining the nature of the interference with the method and bringing this information to the attention of the Director, Environmental Monitoring and Support Laboratory, through the appropriate Quality Assurance Coordinator.

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition. Therefore, as a general rule, it is best to analyze the samples as soon as possible after collection. This is especially true when the analyte concentration is expected to be in the low *ug*/1 range.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing.

The recommended preservative for various constituents is given in Table 1. These choices are based on the accompanying references and on information supplied by various Quality Assurance Coordinators. As more data become available, these recommended holding times will be adjusted to reflect new information. Other information provided in the table is an estimation of the volume of sample required for the analysis, the suggested type of container, and the maximum recommended holding times for samples properly preserved.

TABLE 1

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT[1]

Measurement	Vol. Req. (ml)	Container[2]	Preservative	Holding Time[3]
100 Physical Properties				
Color	50	P,G	Cool, 4°C	24 Hrs.
Conductance	100	P,G	Cool, 4°C	24 Hrs.[4]
Hardness	100	P,G	Cool, 4°C HNO_3 to pH < 2	6 Mos.[5]
Odor	200	G only	Cool, 4°C	24 Hrs.
pH	25	P,G	Det. on site	6 Hrs.
Residue				
Filterable	100	P,G	Cool, 4°C	7 Days
Non-Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	None Req.	24 Hrs.
Temperature	1000	P,G	Det. on site	No Holding
Turbidity	100	P,G	Cool, 4°C	7 Days
200 Metals				
Dissolved	200	P,G	Filter on site HNO_3 to pH < 2	6 Mos.[5]
Suspended	200		Filter on site	6 Mos.
Total	100	P,G	HNO_3 to pH < 2	6 Mos.[5]

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative	Holding Time[3]
Mercury				
Dissolved	100	P,G	Filter on site HNO_3 to pH < 2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P,G	HNO_3 to pH < 2	38 Days (Glass) 13 Days (Hard Plastic)
300 Inorganics, Non-Metallics				
Acidity	100	P,G	None Req	24 Hrs.
Alkalinity	100	P,G	Cool, 4°C	24 Hrs.
Bromide	100	P,G	Cool, 4°C	24 Hrs.
Chloride	50	P,G	None Req.	7 Days
Chlorine	200	P,G	Det. on site	No Holding
Cyanides	500	P,G	Cool, 4°C NaOH to pH 12	24 Hrs.
Fluoride	300	P,G	None Req.	7 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool,4°C H_2SO_4 to pH < 2	24 Hrs.
Kjeldahl, Total	500	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.[6]
Nitrate plus Nitrite	100	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.[6]
Nitrate	100	P,G	Cool, 4°C	24 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative	Holding Time[3]
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	4–8 Hours
Phosphorus				
Ortho-phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	24 Hrs.
Hydrolyzable	50	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.[6]
Total	50	P,G	Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.[6]
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H_2SO_4 to pH < 2	24 Hrs.[6]
Silica	50	P only	Cool, 4°C	7 Days
Sulfate	50	P,G	Cool, 4°C	7 Days
Sulfide	500	P,G	2 ml zinc acetate	24 Hrs.
Sulfite	50	P,G	Det. on site	No Holding
400 Organics				
BOD	1000	P,G	Cool, 4°C	24 Hrs.
COD	50	P,G	H_2SO_4 to pH < 2	7 Days[6]
Oil & Grease	1000	G only	Cool, 4°C H_2SO_4 or HCl to pH < 2	24 Hrs.
Organic carbon	25	P,G	Cool, 4°C H_2SO_4 or HCl to pH < 2	24 Hrs.
Phenolics	500	G only	Cool, 4°C H_3PO_4 to pH < 4 1.0 g $CuSO_4$/l	24 Hrs.
MBAS	250	P,G	Cool, 4°C	24 Hrs.

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container[2]	Preservative	Holding Time[3]
NTA	50	P,G	Cool, 4°C	24 Hrs.

1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72–82 (1976) Method D-3370.

2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.

3. It should be pointed out that holding times listed above are recommended for properly preserved samples based on currently available data. It is recognized that for some sample types, extension of these times may be possible while for other types, these times may be too long. Where shipping regulations prevent the use of the proper preservation technique or the holding time is exceeded, such as the case of a 24-hour composite, the final reported data for these samples should indicate the specific variance.

4. If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.

5. Where HNO_3 cannot be used because of shipping restrictions, the sample may be initially preserved by icing and immediately shipped to the laboratory. Upon receipt in the laboratory, the sample must be acidified to a pH <2 with HNO_3 (normally 3 ml 1:1 HNO_3/liter is sufficient). At the time of analysis, the sample container should be thoroughly rinsed with 1:1 HNO_3 and the washings added to the sample (volume correction may be required).

6. Data obtained from National Enforcement Investigations Center-Denver, Colorado, support a four-week holding time for this parameter in Sewerage Systems. (SIC 4952).

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pH

Method 150.1 (Electrometric)

STORET NO.
Determined on site 00400
Laboratory 00403

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
2. Summary of Method
   2.1 The pH of a sample is determined electrometrically using either a glass electrode in combination with a reference potential or a combination electrode.
3. Sample Handling and Preservation
   3.1 Samples should be analyzed as soon as possible preferably in the field at the time of sampling.
   3.2 High-purity waters and waters not at equilibrium with the atmosphere are subject to changes when exposed to the atmosphere, therefore the sample containers should be filled completely and kept sealed prior to analysis.
4. Interferences
   4.1 The glass electrode, in general, is not subject to solution interferences from color, turbidity, colloidal matter, oxidants, reductants or high salinity.
   4.2 Sodium error at pH levels greater than 10 can be reduced or eliminated by using a "low sodium error" electrode.
   4.3 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.
   4.4 Temperature effects on the electrometric measurement 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 is the change of pH inherent in the sample at various temperatures. 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.
5. Apparatus
   5.1 pH Meter-laboratory or field model. A wide variety of instruments are commercially available with various specifications and optional equipment.

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5.2 Glass electrode.

5.3 Reference electrode–a calomel, silver-silver chloride or other reference electrode of constant potential may be used.

NOTE 1: Combination electrodes incorporating both measuring and reference functions are convenient to use and are available with solid, gel type filling materials that require minimal maintenance.

5.4 Magnetic stirrer and Teflon-coated stirring bar.

5.5 Thermometer or temperature sensor for automatic compensation.

6. Reagents

6.1 Primary standard buffer salts are available from the National Bureau of Standards and should be used in situations where extreme accuracy is necessary.

6.1.1 Preparation of reference solutions from these salts require some special precautions and handling[1] such as low conductivity dilution water, drying ovens, and carbon dioxide free purge gas. These solutions should be replaced at least once each month.

6.2 Secondary standard buffers may be prepared from NBS salts or purchased as a solution from commercial vendors. Use of these commercially available solutions, that have been validated by comparison to NBS standards, are recommended for routine use.

7. Calibration

7.1 Because of the wide variety of pH meters and accessories, detailed operating 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.

7.2 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.

7.2.1 Various instrument designs may involve use of a "balance" or "standardize" dial and/or a slope adjustment as outlined in the manufacturer's instructions. Repeat adjustments on successive portions of the two buffer solutions as outlined in procedure 8.2 until readings are within 0.05 pH units of the buffer solution value.

8. Procedure

8.1 Standardize the meter and electrode system as outlined in Section 7.

8.2 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.

8.2.1 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 insure sufficient sample movement across the electrode sensing element as indicated by drift free (< 0.1 pH) readings.

8.3 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

[1]National Bureau of Standards Special Publication 260.

compensators that electronically adjust for temperature differences. Refer to manufacturer's instructions.

8.4 After rinsing and gently wiping the electrodes, if necessary, immerse them into the sample beaker or sample stream and stir at a constant rate to provide homogeneity and suspension of solids. Rate of stirring should minimize the air transfer rate at the air water interface of the sample. 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.

9. Calculation

9.1 pH meters read directly in pH units. Report pH to the nearest 0.1 unit and temperature to the nearest °C.

10. Precision and Accuracy

10.1 Forty-four analysts in twenty laboratories analyzed six synthetic water samples containing exact increments of hydrogen-hydroxyl ions, with the following results:

pH Units	Standard Deviation pH Units	Accuracy as Bias, %	Accuracy as Bias, pH Units
3.5	0.10	–0.29	–0.01
3.5	0.11	–0.00	
7.1	0.20	+1.01	+0.07
7.2	0.18	–0.03	–0.002
8.0	0.13	–0.12	–0.01
8.0	0.12	+0.16	+0.01

(FWPCA Method Study 1, Mineral and Physical Analyses)

10.2 In a single laboratory (EMSL), using surface water samples at an average pH of 7.7, the standard deviation was ±0.1.

Bibliography

1. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 460, (1975).
2. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293–65, p 178 (1976).

METALS

(Atomic Absorption Methods)

1. Scope and Application

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes. While drinking waters free of particulate matter may be analyzed directly, domestic and industrial wastes require processing to solubilize suspended material. Sludges, sediments and other solid type samples may also be analyzed after proper pretreatment.

1.2 Detection limits, sensitivity and optimum ranges of the metals will vary with the various makes and models of satisfactory atomic absorption spectrophotometers. The data shown in Table 1, however, provide some indication of the actual concentration ranges measurable by direct aspiration and using furnace techniques. In the majority of instances the concentration range shown in the table by direct aspiration may be extended much lower with scale expansion and conversely extended upwards by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. Lower concentrations may also be determined using the furnace techniques. The concentration ranges given in Table 1 are somewhat dependent on equipment such as the type of spectrophotometer and furnace accessory, the energy source and the degree of electrical expansion of the output signal. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To insure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see 5.2.1) and if detected, treat accordingly using either successive dilution, matrix modification or method of standard additions (see 8.5).

1.3 Where direct aspiration atomic absorption techniques do not provide adequate sensitivity, in addition to the furnace procedure, reference is made to specialized procedures such as the gaseous hydride method for arsenic and selenium, the cold vapor technique for mercury, and the chelation–extraction procedure for selected metals. Reference to approved colorimetric methods is also made.

1.4 Atomic absorption procedures are provided as the methods of choice; however, other instrumental methods have also been shown to be capable of producing precise and accurate analytical data. These instrumental techniques include emission spectroscopy, X-ray fluorescence, spark source mass spectroscopy, and anodic stripping to name but a few. The analyst should be cautioned that these methods are highly specialized techniques requiring a high degree of skill to interpret results and obtain valid data.

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These above mentioned techniques are presently considered as alternate test procedures and approval must be obtained prior to their use.

2. Summary of Method

2.1 In direct aspiration atomic absorption spectroscopy a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp whose cathode is made of the element to be determined is directed through the flame into a monochromator, and onto a detector that measures the amount of light absorbed. Absorption depends upon the presence of free unexcited ground state atoms in the flame. Since the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.2 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy (Spectrochim Acta, *24B* 53, 1969) the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2.1 Preliminary treatment of wastewater and/or industrial effluents is usually necessary because of the complexity and variability of the sample matrix. Suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. When the breakdown of organic material is necessitated, the process should include a wet digestion with nitric acid.

2.2.2 In those instances where complete characterization of a sample is desired, the suspended material must be analyzed separately. This may be accomplished by filtration and acid digestion of the suspended material. Metallic constituents in this acid digest are subsequently determined and the sum of the dissolved plus suspended concentrations will then provide the total concentrations present. The sample should be filtered as soon as possible after collection and the filtrate acidified immediately.

2.2.3 The total sample may also be treated with acid without prior filtration to measure what may be termed "total recoverable" concentrations.

2.3 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms are vaporized and dissociated for absorption in the tube than the flame, the use of small sample volumes or detection of low concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption except a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground state element in the vapor.

TABLE 1

Atomic Absorption Concentration Ranges[1]

	Direct Aspiration				Furnace Procedure[4,5]			
Metal	Detection Limit mg/l	Sensitivity mg/l	Optimum Concentration Range mg/l		Detection Limit ug/l	Optimum Concentration Range ug/l		
Aluminum	0.1	1	5	– 50	3	20	–	200
Antimony	0.2	0.5	1	– 40	3	20	–	300
Arsenic[2]	0.002	–	0.002	– 0.02	1	5	–	100
Barium(p)	0.1	0.4	1	– 20	2	10	–	200
Beryllium	0.005	0.025	0.05	– 2	0.2	1	–	30
Cadmium	0.005	0.025	0.05	– 2	0.1	0.5	–	10
Calcium	0.01	0.08	0.2	– 7	–	–		–
Chromium	0.05	0.25	0.5	– 10	1	5	–	100
Cobalt	0.05	0.2	0.5	– 5	1	5	–	100
Copper	0.02	0.1	0.2	– 5	1	5	–	100
Gold	0.1	0.25	0.5	– 20	1	5	–	100
Iridium(p)	3	8	20	– 500	30	100	–	1500
Iron	0.03	0.12	0.3	– 5	1	5	–	100
Lead	0.1	0.5	1	– 20	1	5	–	100
Magnesium	0.001	0.007	0.02	– 0.5	–	–		–
Manganese	0.01	0.05	0.1	– 3	0.2	1	–	30
Mercury[3]	0.0002	–	0.0002	– 0.01	–	–		–
Molybdenum(p)	0.1	0.4	1	– 40	1	3	–	60
Nickel(p)	0.04	0.15	0.3	– 5	1	5	–	100
Osmium	0.3	1	2	– 100	20	50	–	500
Palladium(p)	0.1	0.25	0.5	– 15	5	20	–	400
Platinum(p)	0.2	2	5	– 75	20	100	–	2000
Potassium	0.01	0.04	0.1	– 2	–	–		
Rhenium(p)	5	15	50	– 1000	200	500	–	5000
Rhodium(p)	0.05	0.3	1	– 30	5	20	–	400
Ruthenium	0.2	0.5	1	– 50	20	100	–	2000
Selenium[2]	0.002	–	0.002	– 0.02	2	5	–	100
Silver	0.01	0.06	0.1	– 4	0.2	1	–	25
Sodium	0.002	0.015	0.03	– 1	–	–		–
Thallium	0.1	0.5	1	– 20	1	5	–	100
Tin	0.8	4	10	– 300	5	20	–	300
Titanium (p)	0.4	2	5	– 100	10	50	–	500
Vanadium (p)	0.2	0.8	2	– 100	4	10	–	200
Zinc	0.005	0.02	0.05	– 1	0.05	0.2	–	4

(1) The concentrations shown are not contrived values and should be obtainable with any satisfactory atomic absorption spectrophotometer.

(2) Gaseous hydride method.

(3) Cold vapor technique.

(4) For furnace sensitivity values consult instrument operating manual.

(5) The listed furnace values are those expected when using a 20 *ul* injection and normal gas flow except in the case of arsenic and selenium where gas interrupt is used. The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

3. Definition of Terms
   - 3.1 Optimum Concentration Range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating condition employed.
   - 3.2 Sensitivity: The concentration in milligrams of metal per liter that produces an absorption of 1%.
   - 3.3 Detection Limit: Detection limits can be expressed as either an instrumental or method parameter. The limiting factor of the former using acid water standards would be the signal to noise ratio and degree of scale expansion used; while the latter would be more affected by the sample matrix and preparation procedure used. The Scientific Apparatus Makers Association (SAMA) has approved the following definition for detection limit: that concentration of an element which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution, the concentraton of which is distinctly detectable above, but close to blank absorbance measurement. The detection limit values listed in Table I and on the individual analysis sheets are to be considered minimum working limits achievable with the procedures given in this manual. These values may differ from the optimum detection limit reported by the various instrument manufacturers.
   - 3.4 Dissolved Metals: Those constituents (metals) which will pass through a 0.45 u membrane filter.
   - 3.5 Suspended Metals: Those constituents (metals) which are retained by a 0.45 u membrane filter.
   - 3.6 Total Metals: The concentration of metals determined on an unfiltered sample following vigorous digestion (Section 4.1.3), or the sum of the concentrations of metals in both the dissolved and suspended fractions.
   - 3.7 Total Recoverable Metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Section 4.1.4).

4. Sample Handling and Preservation
   - 4.1 For the determination of trace metals, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus which the sample contacts are all sources of potential contamination. For liquid samples, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention. The sample bottle whether borosilicate glass, linear polyethylene, polyproplyene or Teflon should be thoroughly washed with detergent and tap water; rinsed with 1:1 nitric acid,

tap water, 1:1 hydrochloric acid, tap water and finally deionized distilled water in that order.

NOTE 1: Chromic acid may be useful to remove organic deposits from glassware; however, the analyst should be cautioned that the glassware must be thoroughly rinsed with water to remove the last traces of chromium. This is especially important if chromium is to be included in the analytical scheme. A commercial product—NOCHROMIX—available from Godax Laboratories, 6 Varick St. New York, N.Y. 10013, may be used in place of chromic acid. [Chromic acid should not be used with plastic bottles.]

NOTE 2: If it can be documented through an active analytical quality control program using spiked samples, reagent and sample blanks, that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

Before collection of the sample a decision must be made as to the type of data desired, i.e., dissolved, suspended, total or total recoverable. For container preference, maximum holding time and sample preservation at time of collection see Table 1 in the front part of this manual. Drinking water samples containing suspended and setteable material should be prepared using the total recoverable metal procedure (section 4.1.4).

4.1.1 For the determination of dissolved constituents the sample must be filtered through a 0.45 u membrane filter as soon as practical after collection. (Glass or plastic filtering apparatus using plain, non-grid marked, membrane filters are recommended to avoid possible contamination.) Use the first 50–100 ml to rinse the filter flask. Discard this portion and collect the required volume of filtrate. Acidify the filtrate with 1:1 redistilled HNO_3 to a pH of <2. Normally, 3 ml of (1:1) acid per liter should be sufficient to preserve the sample (See Note 3). If hexavalent chromium is to be included in the analytical scheme, a portion of the filtrate should be transferred before acidification to a separate container and analyzed as soon as possible using Method 218.3. Analyses performed on a sample so treated shall be reported as "dissolved" concentrations.

NOTE 3: If a precipitate is formed upon acidification, the filtrate should be digested using 4.1.3. Also, it has been suggested (International Biological Program, Symposium on Analytical Methods, Amsterdam, Oct. 1966) that additional acid, as much as 25 ml of conc. HCl/liter, may be required to stabilize certain types of highly buffered samples if they are to be stored for any length of time. Therefore, special precautions should be observed for preservation and storage of unusual samples intended for metal analysis.

4.1.2 For the determination of suspended metals a representative volume of unpreserved sample must be filtered through a 0.45 *u* membrane filter. When considerable suspended material is present, as little as 100 ml of a well mixed sample is filtered. Record the volume filtered and transfer the membrane filter containing the insoluble material to a 250 ml Griffin beaker and add 3 ml conc. redistilled HNO_3. Cover the beaker with a watch glass and heat gently. The warm acid will soon dissolve the membrane. Increase the temperature of the hot plate and digest the material. When the acid has nearly evaporated, cool the beaker and watch glass and add another 3 ml of conc. redistilled HNO_3. Cover and continue heating until

the digestion is complete, generally indicated by a light colored digestate. Evaporate to near dryness (DO NOT BAKE), add 5 ml distilled HCl (1:1) and warm the beaker gently to dissolve any soluble material. (If the sample is to be analyzed by the furnace procedure, 1 ml of 1:1 distilled HNO_3 per 100 ml dilution should be substituted for the distilled 1:1 HCl.) Wash down the watch glass and beaker walls with deionized distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected concentrations of metals present. This volume will vary depending on the metal to be determined. The sample is now ready for analysis. Concentrations so determined shall be reported as "suspended" (See Note 4.)

NOTE 4: Certain metals such as antimony arsenic, gold, iridium, mercury, osmium, palladium, platinium, rhenium, rhodium, ruthenium, selenium, silver, thallium, tin and titanium require modification of the digestion procedure and the individual sheets for these metals should be consulted.

4.1.3 For the determination of total metals the sample is acidified with 1:1 redistilled HNO_3 to a pH of less than 2 at the time of collection. The sample is not filtered before processing. Choose a volume of sample appropriate for the expected level of metals. If much suspended material is present, as little as 50–100 ml of well mixed sample will most probably be sufficient. (The sample volume required may also vary proportionally with the number of metals to be determined.)

Transfer a representative aliquot of the well mixed sample to a Griffin beaker and add 3 ml of conc. redistilled HNO_3. Place the beaker on a hot plate and evaporate to near dryness cautiously, making certain that the sample does not boil. (DO NOT BAKE.) Cool the beaker and add another 3 ml portion of conc. redistilled HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add 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. (If the sample is to be analyzed by the furnace procedure, substitute distilled HNO_3 for 1:1 HCl so that the final dilution contains 0.5% (v/v) HNO_3.) Wash down the beaker walls and watch glass with distilled water and filter the sample to remove silicates and other insoluble material that could clog the atomizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis. Concentrations so determined shall be reported as "total" (see Note 4).

4.1.4 To determine total recoverable metals, acidify the entire sample at the time of collection with conc. redistilled HNO_3, 5 ml/1. At the time of analysis a 100 ml aliquot of well mixed sample is transferred to a beaker or flask. Five ml of distilled HCl (1:1) is added and the sample heated on a steam bath or hot plate until the

volume has been reduced to 15–20 ml making certain the samples do not boil. (If the sample is being prepared for furnace analysis, the same process should be followed except HCl should be omitted.) After this treatment the sample is filtered to remove silicates and other insoluble material that could clog the atomizer and the volume adjusted to 100 ml. The sample is then ready for analysis. Concentrations so determined shall be reported as "total". (See Notes 4, 5, and 6.)

NOTE 5: The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy certain metal complexes if a colorimetric procedure is to be employed for the final determination. When this is suspect, the more vigorous digestion given in 4.1.3 should be followed.

NOTE 6: For drinking water analyses by direct aspiration, the final volume may be reduced to effect up to a 10X concentration of the sample, provided the total dissolved solids in the original sample do not exceed 500 mg/1, the determination is corrected for any non-specific absorbance and there is no loss by precipitation.

5. Interferences

5.1 Direct Aspiration

5.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or because the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome the phosphate interference in the magnesium, calcium and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

5.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. While complexing agents are primarily employed to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

5.1.3 The presence of high dissolved solids in the sample may result in an interference from non-atomic absorbance such as light scattering. If background correction is not available, a non-absorbing wavelength should be checked. Preferably, high solids type samples should be extracted (see 5.1.1 and 9.2).

5.1.4 Ionization interferences occur where the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positive charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess of an easily ionized element.

5.1.5 Although quite rare, spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Also, interference can occur

when resonant energy from another element in a multi-element lamp or a metal impurity in the lamp cathode falls within the bandpass of the slit setting and that metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

5.2 Flameless Atomization

5.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical and matrix interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference use the following procedure. Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. [The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4 while keeping in mind the optimum concentration range of the analysis. Under no circumstances should the dilution be less than 1:1]. The diluted aliquots should then be analyzed and the unspiked results multiplied by the dilution factor should be compared to the original determination. Agreement of the results (within ±10%) indicates the absence of interference. Comparison of the actual signal from the spike to the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis. Those samples which indicate the presence of interference, should be treated in one or more of the following ways.

a. The samples should be successively diluted and reanalyzed to determine if the interference can be eliminated.

b. The matrix of the sample should be modified in the furnace. Examples are the addition of ammonium nitrate to remove alkali chlorides, ammonium phosphate to retain cadmium, and nickel nitrate for arsenic and selenium analyses [ATOMIC ABSORPTION NEWSLETTER Vol. 14, No. 5, p 127, Sept-Oct 1975]. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

c. Analyze the sample by method of standard additions while noting the precautions and limitations of its use (See 8.5).

5.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, either the use of background correction or choosing an alternate wavelength outside the absorption band should eliminate this interference. Non-specific broad band absorption interference can also be compensated for with background correction.

5.2.3 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in

the presence of air. Care must be taken, however, to prevent loss of the analysis element.

5.2.4 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion prior to being placed in the furnace. In this way broad band absorption will be minimized.

5.2.5 From anion interference studies in the graphite furnace it is generally accepted that nitrate is the preferred anion. Therefore nitric acid is preferable for any digestion or solubilization step. If another acid in addition to $HN0_3$ is required a minimum amount should be used. This applies particularly to hydrochloric and to a lesser extent to sulfuric and phosphoric acids.

5.2.6 Carbide formation resulting from the chemical environment of the furnace has been observed with certain elements that form carbides at high temperatures. Molybdenum may be cited as an example. When this takes place, the metal will be released very slowly from the carbide as atomization continues. For molybdenum, one may be required to atomize for 30 seconds or more before the signal returns to baseline levels. This problem is greatly reduced and the sensitivity increased with the use of pyrolytically-coated graphite.

5.2.7 Ionization interferences have to date not been reported with furnace techniques.

5.2.8 For comments on spectral interference see section 5.1.5.

5.2.9 Contamination of the sample can be a major source of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in part 6.9 of the Atomic Absorption Methods section of this manual. Pipet tips have been known to be a source of contamination. If suspected, they should be acid soaked with 1:5 HNO_3 and rinsed thoroughly with tap and deionized water. The use of a better grade pipet tip can greatly reduce this problem. It is very important that special attention be given to reagent blanks in both analysis and the correction of analytical results. Lastly, pyrolytic graphite because of the production process and handling can become contaminated. As many as five to possibly ten high temperature burns may be required to clean the tube before use.

6. Apparatus

6.1 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 interfacing with a strip chart recorder.

6.2 Burner: The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

6.3 Hollow cathode lamps: Single element lamps are to be preferred but multi-element lamps may be used. Electrodeless discharge lamps may also be used when available.

6.4 Graphite furnace: Any furnace device capable of reaching the specified temperatures is satisfactory.

6.5 Strip chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can be easily recognized.

6.6 Pipets: Microliter with disposable tips. Sizes can range from 5 to 100 microliters as required. **NOTE 7**: Pipet tips which are white in color, do not contain CdS, and have been found suitable for research work are available from Ulster Scientific, Inc. 53 Main St. Highland, NY 12528 (914) 691–7500.

6.7 Pressure-reducing valves: The supplies of fuel and oxidant shall be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

6.8 Separatory flasks: 250 ml, or larger, for extraction with organic solvents.

6.9 Glassware: All glassware, linear polyethylene, polyproplyene or Teflon containers, including sample bottles, should be washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and deionized distilled water in that order. [See Notes 1 and 2 under (4.1) concerning the use of chromic acid and the cleaning procedure.]

6.10 Borosilicate glass distillation apparatus.

7. Reagents

7.1 Deionized distilled water: Prepare by passing distilled water through a mixed bed of cation and anion exchange resins. Use deionized distilled water for the preparation of all reagents, calibration standards, and as dilution water.

7.2 Nitric acid (conc.): If metal impurities are found to be present, distill reagent grade nitric acid in a borosilicate glass distillation apparatus or use a spectrograde acid.

Caution: Distillation should be performed in hood with protective sash in place.

7.2.1 Nitric Acid (1:1): Prepare a 1:1 dilution with deionized, distilled water by adding the conc. acid to an equal volume of water.

7.3 Hydrochloric acid (1:1): Prepare a 1:1 solution of reagent grade hydrochloric acid and deionized distilled water. If metal impurities are found to be present, distill this mixture from a borosilicate glass distillation apparatus or use a spectrograde acid.

7.4 Stock standard metal solutions: Prepare as directed in (8.1) and under the individual metal procedures. Commercially available stock standard solutions may also be used.

7.5 Calibration standards: Prepare a series of standards of the metal by dilution of the appropriate stock metal solution to cover the concentration range desired.

7.6 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or from a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

7.7 Special reagents for the extraction procedure.

7.7.1 Pyrrolidine dithiocarbamic acid (PDCA) "see footnote": Prepare by adding 18 ml of analytical reagent grade pyrrolidine to 500 ml of chloroform in a liter flask.

The name pyrrolidine dithiocarbamic acid (PDCA), although commonly referenced in the scientific literature is ambiguous. From the chemical reaction of pyrrolidine and carbon disulfide a more proper name would be 1-pyrrolidine carbodithioic acid, PCDA (CAS Registry No. 25769–03–3).

(See **Note 8**) Cool and add 15 ml of carbon disulfide in small portions and with swirling. Dilute to 1 liter with chloroform. The solution can be used for several months if stored in a brown bottle in a refrigerator.

NOTE 8: An acceptable grade of pyrrolidine may be obtained from the Aldrich Chemical Co., 940 West St. Paul Ave., Milwaukee, WI. 53233 (414, 273–3850).

7.7.2 Ammonium hydroxide, 2N: Dilute 3 ml conc. NH_4OH to 100 ml with deionized distilled water.

7.7.3 Bromphenol blue indicator (1g/liter): Dissolve 0.1g bromphenol blue in 100 ml of 50 percent ethanol or isopropanol.

7.7.4 HCl, 2.5% v/v: Dilute 2 ml redistilled HCl to 40 ml with deionized distilled water.

8. Preparation of Standards and Calibration

8.1 Stock standard solutions are prepared from high purity metals, oxides or nonhygroscopic reagent grade salts using deionized distilled water and redistilled nitric or hydrochloric acids. (See individual analysis sheets for specific instruction.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1000 mg of the metal per liter. Commercially available standard solutions may also be used.

8.2 Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time an analysis is to be made and discarded after use. Prepare a blank and at least four calibration standards in graduated amounts in the appropriate range. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. As filtered water samples are preserved with 1:1 redistilled HNO_3 (3 ml per liter), calibration standards for these analyses should be similarly prepared with HNO_3. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal.

8.3 Where the sample matrix is so complex that viscosity, surface tension and components cannot be accurately matched with standards, the method of standard addition must be used. This technique relies on the addition of small, known amounts of the analysis element to portions of the sample—the absorbance difference between those and the original solution giving the slope of the calibration curve. The method of standard addition is described in greater detail in (8.5).

8.4 For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorption of 0 to 80 percent. The correct method is to convert the percent absorption readings to absorbance and plot that value against concentration. The following relationship is used to convert absorption values to absorbance:

$$\text{absorbance} = \log(100/\%T) = 2 - \log \%T$$
$$\text{where } \%T = 100 - \% \text{ absorption}$$

As the curves are frequently nonlinear, especially at high absorption values, the number of standards should be increased in that portion of the curve.

8.5 Method of Standard Additions: In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The volume of the blank and the standards must be the same. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Fig. 1.

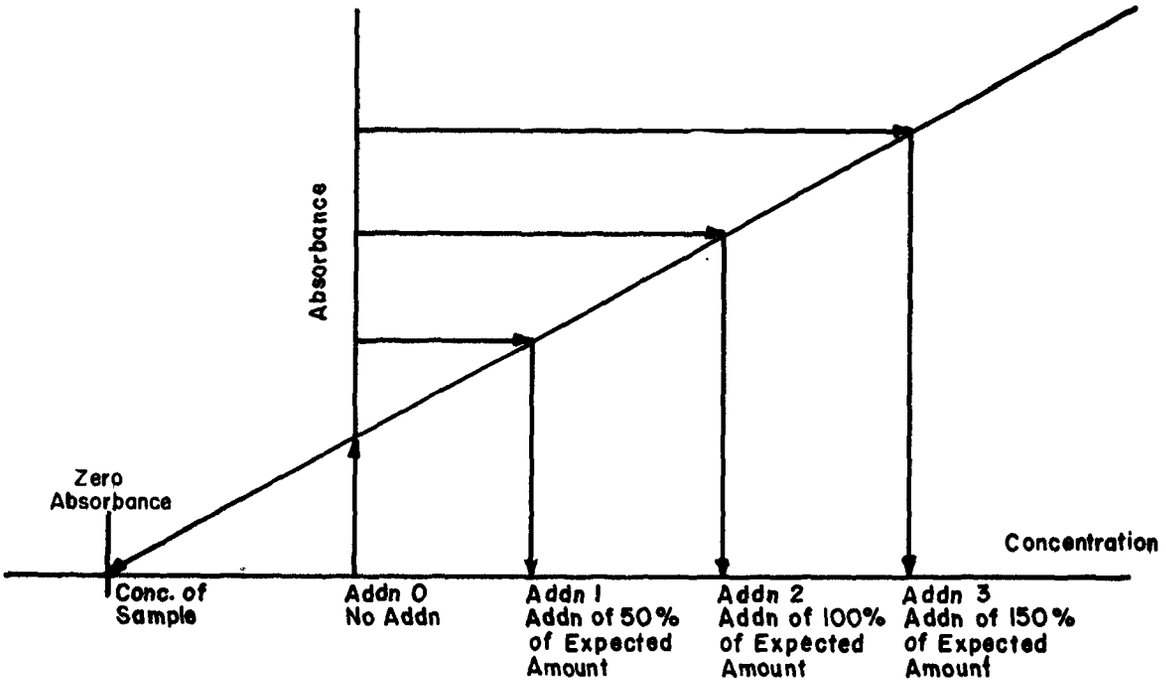

FIGURE 1. STANDARD ADDITION PLOT

The method of standard additions can be very useful, however, for the results to be valid the following limitations must be taken into consideration:

a) the absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b) the effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

c) the determination must be free of spectral interference and corrected for non-specific background interference.

9. General Procedure for Analysis by Atomic Absorption

9.1 Direct Aspiration: Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufactuerer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

9.1.1 Calculation - Direct determination of liquid samples: Read the metal value in mg/l from the calibration curve or directly from the readout system of the instrument.

9.1.1.1 If dilution of sample was required:

$$\text{mg/l metal in sample} = A \left(\frac{C + B}{C} \right)$$

where:

A = mg/l of metal indiluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.1.2 For samples containing particulates:

$$\text{mg/l metal in sample} = A\left(\frac{V}{C}\right)$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
C = ml of sample aliquot processed

9.1.3 For solid samples: report all concentrations as mg/kg dry weight

9.1.3.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{D}$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
D = weight of dry sample in grams

9.1.3.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{W \times P}$$

where:

A = mg/l of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
W = weight of wet sample in grams
P = % solids

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) (see footnote) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. This procedure is described under method 218.3.

The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium, 1-pyrollidine carbodithioate (APCD), CAS Registry No. 5108-96-3.

Aluminum, beryllium, barium and strontium also do not react with APDC. While the **APDC-MIBK** chelating-solvent system can be used satisfactorily, it is possible to experience difficulties. (See Note 9.)

NOTE 9: Certain metal chelates, manganese-APDC in particular, are not stable in MIBK and will redissolve into the aqueous phase on standing. The extraction of other metals is sensitive to both shaking rate and time. As with cadmium, prolonged extraction beyond 1 minute, will reduce the extraction efficiency, whereas 3 minutes of vigorous shaking is required for chromium.

Also, when multiple metals are to be determined either larger sample volumes must be extracted or individual extractions made for each metal being determined. The acid form of APDC-pyrrolidine dithiocarbamic acid prepared directly in chloroform as described by Lakanen, [Atomic Absorption Newsletter *5*, p 17 (1966)], (see 7.7.1) has been found to be most advantageous. In this procedure the more dense chloroform layer allows for easy combination of multiple extractions which are carried out over a broader pH range favorable to multielement extractions. Pyrrolidine dithiocarbamic acid in chloroform is very stable and may be stored in a brown bottle in the refrigerator for months. Because chloroform is used as the solvent, it may not be aspirated into the flame. The following procedure is suggested.

9.2.1 Extraction procedure with pyrrolidine dithiocarbamic acid (PDCA) in chloroform.

9.2.1.1 Transfer 200 ml of sample into a 250 ml separatory funnel, add 2 drops bromphenol blue indicator solution (7.7.3) and mix.

9.2.1.2 Prepare a blank and sufficient standards in the same manner and adjust the volume of each to approximately 200 ml with deionized distilled water. All of the metals to be determined may be combined into single solutions at the appropriate concentration levels.

9.2.1.3 Adjust the pH by addition of 2N NH_4OH solution (7:7.2) until a blue color persists. Add HCl (7.7.4) dropwise until the blue color just disappears; then add 2.0 ml HCl (7.7.4) in excess. The pH at this point should be 2.3. (The pH adjustment may be made with a pH meter instead of using indicator.)

9.2.1.4 Add 5 ml of PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and drain the chloroform layer into a 100 ml beaker. (See NOTE 10.)

NOTE 10: If hexavalent chromium is to be extracted, the aqueous phase must be readjusted back to a pH of 2.3 after the addition of PDCA–chloroform and maintained at that pH throughout the extraction. For multielement extraction, the pH may adjusted upward after the chromium has been extracted.

9.2.1.5 Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (9.2.1.4).

9.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.

9.2.1.7 Repeat step (9.2.1.4) again combining the solvent extracts.

9.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.

9.2.1.9 Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.

9.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.

9.2.1.11 Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard (*ug/l*) in the 200 ml extracted standard solution. To calculate sample concentration read the metal value in *ug/l* from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required use the following equation:

$$\text{mg/l metal in sample} = Z\left(\frac{C + B}{C}\right)$$

where:

Z = *ug/l* of metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3 Furnace Procedure: Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instuctions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100. In addition, the following points may be helpful.

9.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particules, or smoke in the sample

beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

9.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.

9.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.

9.3.4 Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly lessen matrix effects.

9.3.5 Inject a measured microliter 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.

9.3.6 To verify the absence of interference, follow the procedure as given in part 5.2.1.

9.3.7 A check standard should be run approximately after 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. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.

9.3.8 Calculation–For determination of metal concentration by the furnace: Read the metal value in *ug*/l from the calibration curve or directly from the readout system of the instrument.

9.3.8.1 If different size furnace injection volumes are used for samples than for standards:

$$\text{ug/l of metal in sample} = Z \left(\frac{S}{U}\right)$$

where:

Z = *ug*/l of metal read from calibration curve or readout system
S = ul volume standard injected into furnace for calibration curve
U = ul volume of sample injected for analysis

9.3.8.2 If dilution of sample was required but sample injection volume same as for standard:

$$\mu g/l \text{ of metal in sample} = Z \left(\frac{C + B}{C}\right)$$

where:

Z = $\mu g/l$ metal in diluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.3.9 For sample containing particulates:

$$\mu g/l \text{ of metal in sample} = Z \left(\frac{V}{C}\right)$$

where:

Z = $\mu g/l$ of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
C = ml of sample aliquot processed

9.3.10 For solid samples: Report all concentrations as mg/kg dry weight

9.3.10.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1,000}\right) V}{D}$$

where:

Z = $\mu g/l$ of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
D = weight of dry sample in grams

9.3.10.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{\left(\frac{Z}{1,000}\right) V}{W \times P} .$$

where:

Z = $\mu g/l$ of metal in processed sample from calibration curve (See 9.3.8.1)
V = final volume of processed sample in ml
W = weight of wet sample in grams
P = % solids

10 Quality Control For Drinking Water Analysis

10.1 Minimum requirements

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

10.1.2 An unknown performance sample (when available) must be analyzed once per year for the metals measured. Results must be within the control limit established by EPA. If problems arise, they should be corrected, and a follow-up performance sample should be analyzed.

10.2 Minimum Daily control

10.2.1 After a calibration curve composed of a minimum of a reagent blank and three standards has been prepared, subsequent calibration curves must be verified by use of at least a reagent blank and one standard at or near the MCL. Daily checks must be within ±10 percent of original curve.

10.2.2 If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the MCL every 20 samples. Checks must be within ±10 percent of original curve.

10.3 Optional Requirements

10.3.1 A current service contract should be in effect on balances and the atomic absorption spectrophotometer.

10.3.2 Class S weights should be available to make periodic checks on balances.

10.3.3 Chemicals should be dated upon receipt of shipment and replaced as needed or before shelf life has been exceeded.

10.3.4 A known reference sample (when available) should be analyzed once per quarter for the metals measured. The measured value should be within the control limits established by EPA.

10.3.5 At least one duplicate sample should be run every 10 samples, or with each set of samples to verify precision of the method. Checks should be within the control limit established by EPA.

10.3.6 Standard deviation should be obtained and documented for all measurements being conducted.

10.3.7 Quality Control charts or a tabulation of mean and standard deviation should be used to document validity of data on a daily basis.

ANTIMONY

Method 204.1 (Atomic absorption, direct aspiration)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 1–40 mg/l using a wavelength of 217.6 nm
Sensitivity: 0.5 mg/l
Detection Limit: 0.2 mg/l

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in deionized distilled water. Dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Sb (1000 mg/l).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Antimony hollow cathode lamp
2. Wavelength: 217.6 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Fuel lean

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. In the presence of lead (1000 mg/1), a spectral interference may occur at the 217.6 nm resonance line. In this case the 231.1 nm antimony line should be used.
2. Increasing acid concentrations decrease antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

Notes

1. Data to be entered into **STORET** must be reported as *ug*/1.
2. For concentrations of antimony below 0.35 mg/1, the furnace procedure (Method 204.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 5.0 and 15 mg Sb/1, the standard deviations were ±0.08 and ±0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

ANTIMONY

Method 204.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01097
Dissolved 01095
Suspended 01096

Optimum Concentration Range: 20–300 *ug/l*
Detection Limit: 3 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.2% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual should be followed including the addition of sufficient 1:1 HCl to dissolve the digested residue for the analysis of suspended or total antimony. The sample solutions used for analysis should contain 2% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–800°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 217.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. If chloride concentration presents a matrix problem or causes a loss previous to atomization, add an excess of 5 mg of ammonium nitrate to the furnace and ash using a ramp accessory or with incremental steps until the recommended ashing temperature is reached.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

ARSENIC

Method 206.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Dissolve 1.320 g of arsenic trioxide, As_2O_3 (analytical reagent grade) in 100 ml of deionized distilled water containing 4 g NaOH. Acidify the solution with 20 ml conc. HNO_3 and dilute to 1 liter. 1 ml = 1 mg As (1000 mg/1).

2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100ml.

3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.

4. Working Arsenic Solution: 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. HNO_3, 2ml of 30% H_2O_2 and 2ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.

2. Cool and bring back to 50 ml with deionized distilled water.

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 deionized distilled water. The sample is now ready for injection into the furnace.

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Issued 1978

NOTE: If solubilization or digestion is not required, adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30%H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1100°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 193.7 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
4. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent containing 15 *ug*/1 and spiked with concentrations of 2, 10 and 25 *ug*/1, recoveries of 85%, 90% and 88% were obtained respectively. The relative standard deviation at these concentrations levels were ±8.8%, ±8.2%, ±5.4% and ±8.7%, respectively.
2. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 20, 50 and 100 *ug* As/1, the standard deviations were ±0.7, ±1.1 and ±1.6 respectively. Recoveries at these levels were 105%, 106% and 101%, respectively.

ARSENIC

Method 206.3 (Atomic Absorption—gaseous hydride)

STORET NO. Total 01002
Dissolved 01000
Suspended 01001

1. Scope and Application
   1.1 The gaseous hydride method determines inorganic arsenic when present in concentrations at or above 2 *ug/1*. The method is applicable to drinking water and most fresh and saline waters in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
   2.1 Arsenic in the sample is first reduced to the trivalent form using $SnCl_2$ and converted to arsine, AsH_3, using zinc metal. The gaseous hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the mehtod is 2–20 *ug/1*. The 193.7 nm wavelength line is used.
3. Comments
   3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of arsenic to establish adequate recovery.
   3.2 Organic forms of arsenic must be converted to inorganic compounds and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in Method 206.5 (Standard Methods, 14th Edition, Method 404B, p. 285, Procedure 4.a) has been found suitable.
   3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
   3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
   3.5 Data to be entered into **STORET** must be reported as *ug/1*.
4. Precision and Accuracy
   4.1 Ten replicate solutions of o-arsenilic acid at the 5, 10 and 20 *ug/1* level were analyzed by a single laboratory. Standard deviations were ±0.3, ±0.9 and ±1.1 with recoveries of 94, 93 and 85%, respectively. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA., vol 65, p 731, Nov., 1973.)

Approved for NPDES and SDWA
Issued 1974

5. References

5.1. Except for the perchloric acid step, the procedure to be used for this determination is found in: Standard Methods for the Examination of Water and Wastewater, 14th Edition, p159, Method 301A(VII),(1975)

BARIUM

Method 208.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 1–20 mg/l using a wavelength of 553.6 nm
Sensitivity: 0.4 mg/l
Detection Limit: 0.1 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$, analytical reagent grade) in deionized distilled water and dilute to 1 liter. 1 ml = 1 mg Ba (1000 mg/l).
2. Potassium chloride solution: Dissolve 95 g potassium chloride, KCl, in deionized distilled water and make up to 1 liter.
3. Prepare dilutions of the stock barium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml potassium chloride solution. The calibration standards should be prepared using the same type of acid and the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Barium hollow cathode lamp
2. Wavelength: 553.6 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Approved for NPDES and SDWA
Issued 1974

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Interferences

1. The use of a nitrous oxide-acetylene flame virtually eliminates chemical interference; however, barium is easily ionized in this flame and potassium must be added (1000 mg/1) to standards and samples alike to control this effect.
2. If the nitrous oxide flame is not available and acetylene-air is used, phosphate, silicon and aluminum will severely depress the barium absorbance. This may be overcome by the addition of 2000 mg/1 lanthanum.

Notes

1. Data to be entered into **STORET** must be reported as *u*g/1.
2. For concentrations of barium below 0.2 mg/1, the furnace procedure (Method 208.2) is recommended.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.40 and 2.0 mg Ba/1, the standard deviations were ±0.043 and ±0.13, respectively. Recovereis at these levels were 94% and 113%, respectively.
2. In a round-robin study reported by Standard Methods (13th Edition, p215, method 129A, 1971), three synthetic samples containing barium were analyzed by 13 laboratories. At concentrations of 500, 1000 and 5000 *u*g Ba/1, the reported standard deviations were ±50, ±89 and ±185 *u*g, respectively. The relative error at these concentrations was 8.6%, 2.7% and 1.4%, respectively.

BARIUM

Method 208.2 (Atomic Absorption, furnace technique)

STORET NO. 01007
Dissolved 01005
Suspended 01006

Optimum Concentration Range: 10–200 *ug/1*
Detection Limit: 2 *ug/1*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1200°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 553.6 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and pyrolytic graphite.

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2. The use of halide acid should be avoided.
3. Because of possible chemical interaction, nitrogen should not be used as a purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 500 and 1000 *u*g Ba/1, the standard deviations were ±2.5 and ±2.2 *u*g, respectively. Recoveries at these levels were 96% and 102%, respectively A dilution of 1:10 was required to bring the spikes within the analytical range of the method.

BERYLLIUM

Methods 210.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 0.05–2 mg/1 using a wavelength of 234.9 nm
Sensitivity: 0.025 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock solution: Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in deionized distilled water containing 2 ml conc. nitric acid and dilute to 1 liter. 1 ml = 1 mg Be (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Beryllium hollow cathode lamp
2. Wavelength: 234.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Approved for NPDES
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Interferences

1. Sodium and silicon at concentrations in excess of 1000 mg/1 have been found to severely depress the beryllium absorbance.
2. Bicarbonate ion is reported to interfere; however, its effect is eliminated when samples are acidified to a pH of 1.5.
3. Aluminum at concentrations of 500 *ug*/1 is reported to depress the sensitivity of beryllium [Spectrochim Acta 22, 1325 (1966)].

Notes

1. Data to be entered into **STORET** must be reported as *ug*/1.
2. The "aluminon colorimetric method" may also be used (Standard Methods, 14th Edition, p 177). The minimum detectable concentration by this method is 5 *ug*/1.
3. For concentrations of beryllium below 0.02 mg/1, the furnace procedure (Method 210.2) is recommended.

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.01, 0.05 and 0.25 mg Be/1, the standard deviations were ±0.001, ±0.001 and ±0.002, respectively. Recoveries at these levels were 100%, 98% and 97%, respectively.

BERYLLIUM

Method 210.2 (Atomic Absorption, furnace technique)

STORET NO. 01012
Dissolved 01010
Suspended 01011

Optimum Concentration Range: 1–30 *ug/l*
Detection Limit: 0.2 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2800°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 234.9 nm
6. The operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can

Approved for NPDES
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be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Because of possible chemical interaction and reported lower sensitivity, nitrogen should not be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. Precision and Accuracy data are not available at this time.

CADMIUM

Method 213.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.05–2 mg/1 using a wavelength of 228.8 nm
Sensitivity: 0.025 mg/1
Detection Limit: 0.005 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 2.282 g of cadmium sulfate ($3CdSO_4 \cdot 8H_2O$, analytical reagent grade) and dissolve in deionized distilled water. 1 ml = 1 mg Cd (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 through 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Cadmium hollow cathode lamp
2. Wavelength: 228.8 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. For levels of cadmium below 20 ug/1, either the Special Extraction Procedure given in Part 9.2 of the Atomic Absorption methods section as the furnace technique, Method 213.2 is recommended.
2. Data to be entered into **STORET** must be reported as ug/1.
3. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for cadmium were as follows:

Number of Labs	True Values ug/liter	Mean Value ug/liter	Standard Deviation ug/liter	Accuracy as % Bias
74	71	70	21	-2.2
73	78	74	18	-5.7
63	14	16.8	11.0	19.8
68	18	18.3	10.3	1.9
55	1.4	3.3	5.0	135
51	2.8	2.9	2.8	4.7

CADMIUM

Method 213.2 (Atomic Absorption, furnace technique)

STORET NO. 01027
Dissolved 01025
Suspended 01026

Optimum Concentration Range: 0.5–10 *ug/l*
Detection Limit: 0.1 *ug/l*

Preparation of Standard Solution

1. *Stock solution: Prepare as described under "direct aspiration method".*
2. Ammonium Phosphate solution (40%): Dissolve 40 grams of ammonium phosphate, $(NH_4)2HPO_4$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.
3. Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 ml of standard and sample alike add 2.0 ml of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–1900°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 228.8 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Contamination from the work area is critical in cadmium analysis. Use of pipet tips which are free of cadmium is of particular importance. (See part 5.5.7 of the Atomic Absorption Methods section of this manual.)
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 2.5, 5.0 and 10.0 *u*g Cd/1, the standard deviations were ±0.10, ±0.16 and ±0.33, respectively. Recoveries at these levels were 96%, 99% and 98%, respectively.

CHROMIUM

Method 218.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 0.5–10 mg/1 using a wavelength of 357.9 nm
Sensitivity: 0.25 mg/1
Detection Limit: 0.05 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.923 g of chromium trioxide (CrO_3, reagent grade) in deionized distilled water. When solution is complete, acidify with redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Cr (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Chromium hollow cathode lamp
2. Wavelength: 357.9 nm
3. Fuel: Acetylene
4. Oxidant: Nitrous oxide
5. Type of flame: Fuel rich

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. The following wavelengths may also be used:
   359.3 nm Relative Sensitivity 1.4
   425.4 nm Relative Sensitivity 2
   427.5 nm Relative Sensitivity 3
   428.9 nm Relative Sensitivity 4

2. The fuel rich air–acetylene flame provides greater sensitivity but is subject to chemical and matrix interference from iron, nickel, and other metals. If the analysis is performed in a lean flame the interference can be lessened but the sensitivity will also be reduced.
3. The suppression of both Cr (III) and Cr (VI) absorption by most interfering ions in fuel rich air-acetylene flames is reportedly controlled by the addition of 1% ammonium bifluoride in 0.2% sodium sulfate [Talanta 20, 631 (1973)]. A 1% oxine solution is also reported to be useful.
4. For levels of chromium between 50 and 200 *ug/1* where the air-acetylene flame can not be used or for levels below 50 *ug/1*, either the furnace procedure or the extraction procedure is recommended. See Method 218.2 for the furnace procedure and Method 218.3 for the chelation–extraction procedure.
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into **STORET** must be reported as *ug/1*.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for chromium were as follows:

Number of Labs	True Values *ug/liter*	Mean Value *ug/liter*	Standard Deviation *ug/liter*	Accuracy as % Bias
74	370	353	105	–4.5
76	407	380	128	–6.5
72	74	72	29	–3.1
70	93	84	35	–10.2
47	7.4	10.2	7.8	37.7
47	15.0	16.0	9.0	6.8

CHROMIUM

Method 218.2 (Atomic Absorption, furnace technique)

STORET NO. 01034
Dissolved 01030
Suspended 01031

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Calcium Nitrate Solution: Dissolve 11.8 grams of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade) in deionized distilled water and dilute to 100 ml.1 ml = 20 mg Ca.
3. Prepare dilutions of the stock chromium solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3. To each 100 ml of standard and sample alike, add 1 ml of 30% H_2O_2 and 1 ml of the calcium nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods secton of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% v/v HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–1000°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 357.9 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injecton, continuous flow purge gas and non-pyrolytic graphite.
2. Hydrogen peroxide is added to the acidified solution to convert all chromium to the trivalent state. Calcium is added to a level above 200 mg/1 where its suppressive effect becomes constant up to 1000 mg/1.
3. Background correction may be required if the sample contains high dissolved solids.
4. Nitrogen should not be used as a purge gas because of possible CN band interference.
5. Pipet tips have been reported to be a possible source of contamination. (See part 5.5.7 of the Atomic Absorption Methods section of this manual.)
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as *u*g/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 19, 48, and 77 *u*g Cr/1, the standard deviations were ±0.1, ±0.2, and ±0.8, respectively. Recoveries at these levels were 97%, 101%, and 102%, respectively.

LEAD

Method 239.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 1–20 mg/1 using a wavelength of 283.3 nm
Sensitivity: 0.5 mg/1
Detection Limit: 0.1 mg/1

Preparation of Standard Solution

1. Stock Solution: Carefully weigh 1.599 g of lead nitrate, $Pb(NO_3)_2$ (analytical reagent grade), and dissolve in deionized distilled water. When solution is complete acidify with 10 ml redistilled HNO_3 and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Pb (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Lead hollow cathode lamp
2. Wavelength: 283.3 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Notes

1. The analysis of this metal is exceptionally sensitive to turbulence and absorption bands in the flame. Therefore, some care should be taken to position the light beam in the most stable, center portion of the flame. To do this, first adjust the burner to maximize the absorbance reading with a lead standard. Then, aspirate a water blank and make minute adjustments in the burner alignment to minimize the signal.
2. For levels of lead below 200 *ug*/1, either the Special Extraction Procedure given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 239.2, is recommended.
3. The following lines may also be used:
   217.0 nm Relative Sensitivity 0.4
   261.4 nm Relative Sensitivity 10
4. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
5. Data to be entered into **STORET** must be reported as *ug*/1.

Precision and Accuracy

1. An interlaboratory study on trace metal analyses by atomic absorption was conducted by the Quality Assurance and Laboratory Evaluation Branch of EMSL. Six synthetic concentrates containing varying levels of aluminum, cadmium, chromium, copper, iron, manganese, lead and zinc were added to natural water samples. The statistical results for lead were as follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
74	367	377	128	2.9
74	334	340	111	1.8
64	101	101	46	-0.2
64	84	85	40	1.1
61	37	41	25	9.6
60	25	31	22	25.7

LEAD
Method 239.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01051
Dissolved 01049
Suspended 01050

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Lanthanum Nitrate Solution: Dissolve 58.64 g of ACS reagent grade La_2O_3 in 100 ml conc. HNO_3 and dilute to 1000 ml with deionized distilled water. 1 ml = 50 mg La.
3. Working Lead Solution: Prepare dilutions of the stock lead solution to be used as calibration standards at the time of analysis. Each calibration standard should contain 0.5% (v/v) HNO_3. To each 100 ml of diluted standard add 10 ml of the lanthanum nitrate solution.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.
2. To each 100 ml of prepared sample solution add 10 ml of the lanthanum nitrate solution.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–500°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 283.3 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure in the calculation see "Furnace Procedure", part 9.3 of the Atomic Absorption Methods section of this manual.

Approved for NPDES and SDWA
Issued 1978

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Greater sensitivity can be achieved using the 217.0 nm line, but the optimum concentration range is reduced. The use of a lead electrodeless discharge lamp at this lower wavelength has been found to be advantageous. Also a lower atomization temperature (2400°C) may be preferred.
4. To suppress sulfate interference (up to 1500 ppm) lanthanum is added as the nitrate to both samples and calibration standards. (Atomic Absorption Newsletter Vol. 15, No. 3, p 71, May-June 1976.)
5. Since glassware contamination is a severe problem in lead analysis, all glassware should be cleaned immediately prior to use, and once cleaned, should not be open to the atmosphere except when necessary.
6. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
7. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
8. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
9. Data to be entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 100 *ug* Pb/1, the standard deviations were ±1.3, ±1.6, and ±3.7, respectively. Recoveries at these levels were 88%, 92%, and 95% respectively.

MERCURY
Method 245.1 (Manual Cold Vapor Technique)

STORET NO. Total 7190[illegible]
Dissolved 71890
Suspended 71895

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the cold vapor atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potasssium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in or spiked to a natural system. For distilled water the heat step is not necessary.
   1.3 The range of the method may be varied through instrument and/or recorder expansion. Using a 100 ml sample, a detection limit of 0.2 ug Hg/1 can be achieved; concentrations below this level should be reported as < 0.2 (see Appendix 11.2).
2. Summary of Method
   2.1 The flameless AA procedure is a physical method 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 and recorded in the usual manner.
3. Sample Handling and Preservation
   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection. If only dissolved mercury is to be determined, the sample should be filtered through an all glass apparatus before the acid is added. For total mercury the filtration is omitted.
4. Interference
   4.1 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 mg/1 of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from distilled water.

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Issued 1974

4.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/1 had no effect on recovery of mercury from spiked samples.

4.3 Sea waters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 ml). During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation of 253 nm. Care must be taken to assure 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 the addition of stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from sea water using this technique.

4.4 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run without reagents should determine if this type of interference is present (see Appendix 11.1).

5. Apparatus

5.1 Atomic Absorption Spectrophotometer: (See Note 1) 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.

Note 1: 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.

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4-1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" 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" by 2" cards. One inch 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.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 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.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (see Note 2). The apparatus is assembled as shown in Figure 1.

NOTE 2: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc.: Reagent grade.

6.1.1 Sulfuric acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1.0 liter.

6.2 Nitric Acid, Conc: Reagent grade of low mercury content (See Note 3).

NOTE 3: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

6.3 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.)

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Potassium Persulfate: 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 ml of distilled water.

6.7 Stock Mercury 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 ml = 1 mg Hg.

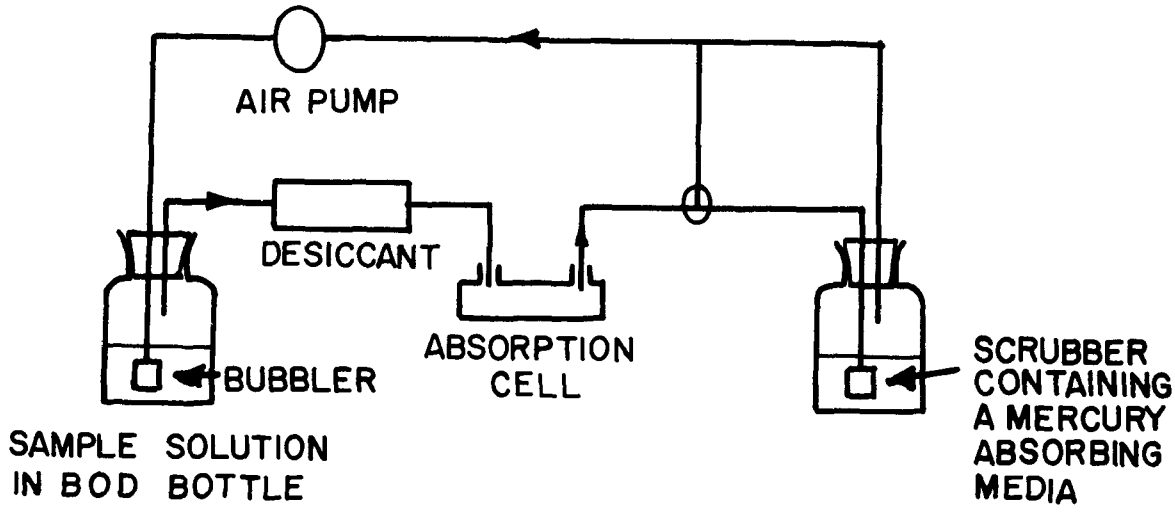

FIGURE 1. APPARATUS FOR FLAMELESS MERCURY DETERMINATION

6.8 Working Mercury Solution: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 *u*g 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 the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10.0 ml aliquots of the working mercury solution containing 0 to 1.0 *u*g of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 100 ml. Mix thoroughly and add 5 ml of conc. sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) to each bottle. Add 15 ml of $KMnO_4$ (6.5) solution to each bottle and allow to stand at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath maintined at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. When the solution has been decolorized wait 30 seconds, add 5 ml of the stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus forming a closed system. 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 per minute, is allowed to run continuously (See Note 4). The absorbance will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 5). Close the bypass valve, remove the stopper and frit from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 4: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 5: Because of the toxic nature of mercury vapor 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:

a) equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4
b) 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.

8. Procedure

8.1 Transfer 100 ml, or an aliquot diluted to 100 ml, containing not more than 1.0 *u*g of mercury, to a 300 ml **BOD** bottle. Add 5 ml of sulfuric acid (6.1) and 2.5 ml of conc. nitric acid (6.2) mixing after each addition. Add 15 ml of potassium permanganate solution (6.5) to each sample bottle. For sewage samples additional permanganate may be required. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 minutes. Add 8 ml of potassium persulfate (6.6) to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6

MERCURY

Method 245.2 (Automated Cold Vapor Technique)

STORET NO. Total 71900
Dissolved 71890
Suspended 71895

1. Scope and Application
   1.1 This method is applicable to surface waters. It may be applicable to saline waters, wastewaters, effluents, and domestic sewages providing potential interferences are not present (See Interference 4).
   1.2 The working range is 0.2 to 20.0 *ug* Hg/1.
2. Summary of Method
   2.1 The flameless AA procedure is a physical method 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. 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 and recorded in the usual manner.
   2.2 In addition to inorganic forms of mercury, organic mercurials may also be present. These organo-mercury compounds will not respond to the flameless atomic absorption technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds but recent studies have shown that a number of organic mercurials, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, an automated persulfate oxidation step following the automated addition of the permanganate has been included to insure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement.
3. Sample Handling and Preservation
   3.1 Until more conclusive data are obtained, samples should be preserved by acidification with nitric acid to a pH of 2 or lower immediately at the time of collection.[1] If only dissolved mercury is to be determined, the sample should be filtered before the acid is added. For total mercury the filtration is omitted.
4. Interference (See **NOTE 1**)
   4.1 Some sea waters and waste-waters high in chlorides have shown a positive interference, probably due to the formation of free chlorine.
   4.2 Interference from certain volatile organic materials which will absorb at this wavelength is also possible. A preliminary run under oxidizing conditions, without stannous sulfate, would determine if this type of interference is present.

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4.3 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.4 Samples containing solids must be blended and then mixed while being sampled if total mercury vlaues are to be reported.

NOTE 1: All the above interferences can be overcome by use of the Manual Mercury method in this manual.

5. Apparatus

5.1 Technicon Auto Analyzer consisting of:

5.1.1 Sampler II with provision for sample mixing.

5.1.2 Manifold.

5.1.3 Proportioning Pump II or III.

5.1.4 High temperature heating bath with two distillation coils (Technicon Part #116-0163) in series.

5.2 Vapor-liquid separator (Figure 1).

5.3 Absorption cell, 100 mm long, 10 mm diameter with quartz windows.

5.4 Atomic Absorption Spectrophotometer (See Note 2): 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.

NOTE 2: 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.

5.5 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.6 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.7 Source of cooling water for jacketed mixing coil and connector A-7.

5.8 Heat lamp: A small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell: The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Sulfuric Acid, Conc: Reagent grade

6.1.1 Sulfuric acid, 2 N: Dilute 56 ml of conc. sulfuric acid to 1 liter with distilled water.

6.1.2 Sulfuric acid, 10%: Dilute 100 ml conc. sulfuric acid to 1 liter with distilled water.

6.2 Nitric acid, Conc: Reagent grade of low mercury content.

6.2.1 Nitric Acid, 0.5% Wash Solution: Dilute 5 ml of conc. nitric acid to 1 liter with distilled water.

6.3 Stannous Sulfate: Add 50 g stannous sulfate to 500 ml of 2 N sulfuric acid (6.1.1). This mixture is a suspension and should be stirred continuously during use.

NOTE 3: Stannous chloride may be used in place of stannous sulfate.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in distilled water to 1 liter.

ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. After a delay of at least 30 seconds add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under Calibration.

9. Calculation

9.1 Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\,Hg/l = \left(\begin{matrix}ug\,Hg\ in \\ aliquot\end{matrix}\right)\left(\frac{1{,}000}{\text{volume of aliquot in ml}}\right)$$

9.3 Report mercury concentrations as follows: Below 0.2 *ug*/1, <0.2; between 1 and 10 *ug*/1, one decimal; above 10 *ug*/1, whole numbers.

10. Precision and Accuracy

10.1 In a single laboratory (EMSL), using an Ohio River composite sample with a background mercury concentration of 0.35 *ug*/1, spiked with concentrations of 1.0, 3.0 and 4.0 *ug*/1, the standard deviations were ±0.14, ±0.10 and ±0.08, respectively. Standard deviation at the 0.35 level was ±0.16. Percent recoveries at the three levels were 89, 87, and 87%, respectively.

10.2 In a joint **EPA/ASTM** interlaboratory study of the cold vapor technique for total mercury in water, increments of organic and inorganic mercury were added to natural waters. Recoveries were determined by difference. A statistical summary of this study follows:

Number of Labs	True Values *ug*/liter	Mean Value *ug*/liter	Standard Deviation *ug*/liter	Accuracy as % Bias
76	0.21	0.349	0.276	66
80	0.27	0.414	0.279	53
82	0.51	0.674	0.541	32
77	0.60	0.709	0.390	18
82	3.4	3.41	1.49	0.34
79	4.1	3.81	1.12	-7.1
79	8.8	8.77	3.69	-0.4
78	9.6	9.10	3.57	-5.2

11. Appendix

11.1 While the possibility of absorption from certain organic substances actually being present in the sample does exist, EMSL has not encountered such samples. This is mentioned only to caution the analyst of the possibility. A simple correction that may be used is as follows: If an interference has been found to be present (4.4), the sample should be analyzed both by using the regular procedure and again under oxidizing conditions only,

that is without the reducing reagents. The true mercury value can then be obtained by subtracting the two values.

11.2 If additional sensitivity is required, a 200 ml sample with recorder expansion may be used provided the instrument does not produce undue noise. Using a Coleman MAS-50 with a drying tube of magnesium perchlorate and a variable recorder, 2 mv was set to read full scale. With these conditions, and distilled water solutions of mercuric chloride at concentrations of 0.15, 0.10, 0.05 and 0.025 *ug/l* the standard deviations were ±0.027, ±0.006, ±0.01 and ±0.004. Percent recoveries at these levels were 107, 83, 84 and 96%, respectively.

11.3 Directions for the disposal of mercury-containing wastes are given in ASTM Standards, Part 31, "Water", p 349, Method D3223 (1976).

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3. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 156 (1975).

NOTE 4: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

6.5 Potassium Permanganate: 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 liter of distilled water.

6.6 Potassium Permanganate, 0.1 N: Dissolve 3.16 g of potassium permanganate in distilled water and dilute to 1 liter.

6.7 Potassium Persulfate: 0.5% solution, w/v. Dissolve 5 g potassium persulfate in 1 liter of distilled water.

6.8 Stock Mercury 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.

6.9 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.8) to obtain a working standard containing 0.1 *ug* 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 the addition of the aliquot. From this solution prepare standards containing 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 *ug* Hg/1.

6.10 Air Scrubber Solution: Mix equal volumes of 0.1 N potassium permanganate (6.6) and 10% sulfuric acid (6.1.2).

7. Procedure

7.1 Set up manifold as shown in Figure 2.

7.2 Feeding all the reagents through the system with acid wash solution (6.2.1) through the sample line, adjust heating bath to 105°C.

7.3 Turn on atomic absorption spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

7.4 Arrange working mercury standards from 0.2 to 20.0 *ug* Hg/1 in sampler and start sampling. Complete loading of sample tray with unknown samples.

7.5 Prepare standard curve by plotting peak height of processed standards against concentration values. Determine concentration of samples by comparing sample peak height with standard curve.

NOTE 5: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Venting the mercury vapor into an exhaust hood or passing the vapor through some absorbing media such as:

a) equal volumes of 0.1 N $KMnO_4$ (6.6) and 10% H_2SO_4 (6.1.2).

b) 0.25% iodine in a 3% KI solution, is recommended.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave. and North Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

7.6 After the analysis is complete put all lines except the H_2SO_4 line in distilled water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (6.3) through the sample lines followed by distilled water. This will prevent build-up of oxides of manganese.

8. Precision and Accuracy

8.1 In a single laboratory (SEWL), using distilled water standards at concentrations of 0.5, 1.0, 2.0, 5.0, 10.0 and 20.0 *ug* Hg/1, the standard deviations were ±0.04, ±0.07, ±0.09, ±0.20, ±0.40 and ±0.84 *ug*/1, respectively.

8.2 In a single laboratory (SEWL), using surface water samples spiked with ten organic mercurials at the 10 *ug*/1 level, recoveries ranged from 87 to 117%. Recoveries of the same ten organic mercurials in distilled water at the 10 *ug*/1 level, ranged from 92% to 125%.

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MERCURY IN SEDIMENT

Method 245.5 (Manual Cold Vapor Technique)

1. Scope and Application
   1.1 This procedure[1] measures total mercury (organic † inorganic) in soils, sediments, bottom deposits and sludge type materials.
   1.2 The range of the method is 0.2 to 5 ug/g. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.
2. Summary of Method
   2.1 A weighed portion of the sample is digested in aqua regia for 2 minutes at 95°C, followed by oxidation with potassium permanganate. Mercury in the digested sample is then measured by the conventional cold vapor technique.
   2.2 An alternate digestion[2] involving the use of an autoclave is described in (8.2).
3. Sample Handling and Preservation
   3.1 Because of the extreme sensitivity of the analytical procedure and the omnipresence of mercury, care must be taken to avoid extraneous contamination. Sampling devices and sample containers should be ascertained to be free of mercury; the sample should not be exposed to any condition in the laboratory that may result in contact or air-borne mercury contamination.
   3.2 While the sample may be analyzed without drying, it has been found to be more convenient to analyze a dry sample. Moisture may be driven off in a drying oven at a temperature of 60°C. No mercury losses have been observed by using this drying step. The dry sample should be pulverized and thoroughly mixed before the aliquot is weighed.
4. Interferences
   4.1 The same types of interferences that may occur in water samples are also possible with sediments, i.e., sulfides, high copper, high chlorides, etc.
   4.2 Volatile materials which absorb at 253.7 nm will cause a positive interference. In order to remove any interfering volatile materials, the dead air space in the **BOD** bottle should be purged before the addition of stannous sulfate.
5. Apparatus
   5.1 Atomic Absorption Spectrophotometer (See Note 1): 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.

   NOTE 1: 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.

Issued 1974

5.2 Mercury Hollow Cathode Lamp: Westinghouse WL-22847, argon filled, or equivalent.

5.3 Recorder: Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

5.4 Absorption Cell: Standard spectrophotometer cells 10 cm long, having quartz end windows may be used. Suitable cells may be constructed from plexiglass tubing, 1" O.D. X 4–1/2". The ends are ground perpendicular to the longitudinal axis and quartz windows (1" diameter X 1/16" thickness) are cemented in place. Gas inlet and outlet ports (also of plexiglass but 1/4" O.D.) are attached approximately 1/2" from each end. The cell is strapped to a burner for support and aligned in the light beam to give the maximum transmittance.

NOTE 2: Two 2" X 2" cards with one inch diameter holes may be placed over each end of the cell to assist in positioning the cell for maximum transmittance.

5.5 Air Pump: Any peristaltic pump capable of delivering 1 liter of air per minute may be used. A Masterflex pump with electronic speed control has been found to be satisfactory. (Regulated compressed air can be used in an open one-pass system.)

5.6 Flowmeter: Capable of measuring an air flow of 1 liter per minute.

5.7 Aeration Tubing: Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return. Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

5.8 Drying Tube: 6" X 3/4" diameter tube containing 20 g of magnesium perchlorate (See Note 3). The apparatus is assembled as shown in the accompanying diagram.

NOTE 3: In place of the magnesium perchlorate drying tube, a small reading lamp with 60W bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient.

6. Reagents

6.1 Aqua Regia: Prepare immediately before use by carefully adding three volumes of conc. HCl to one volume of conc. HNO_3.

6.2 Sulfuric Acid, 0.5 N: Dilute 14.0 ml of conc. sulfuric acid to 1 liter.

6.3 Stannous Sulfate: Add 25 g stannous sulfate to 250 ml of 0.5 N sulfuric acid (6.2). This mixture is a suspension and should be stirred continuously during use.

6.4 Sodium Chloride-Hydroxylamine Sulfate Solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in distilled water and dilute to 100 ml.

NOTE 4: A 10% solution of stannous chloride may be substituted for (6.3) and hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate in (6.4).

6.5 Potassium Permanganate: 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 ml of distilled water.

6.6 Stock Mercury 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.

6.7 Working Mercury Solution: Make successive dilutions of the stock mercury solution (6.6) to obtain a working standard containing 0.1 ug/ml. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the

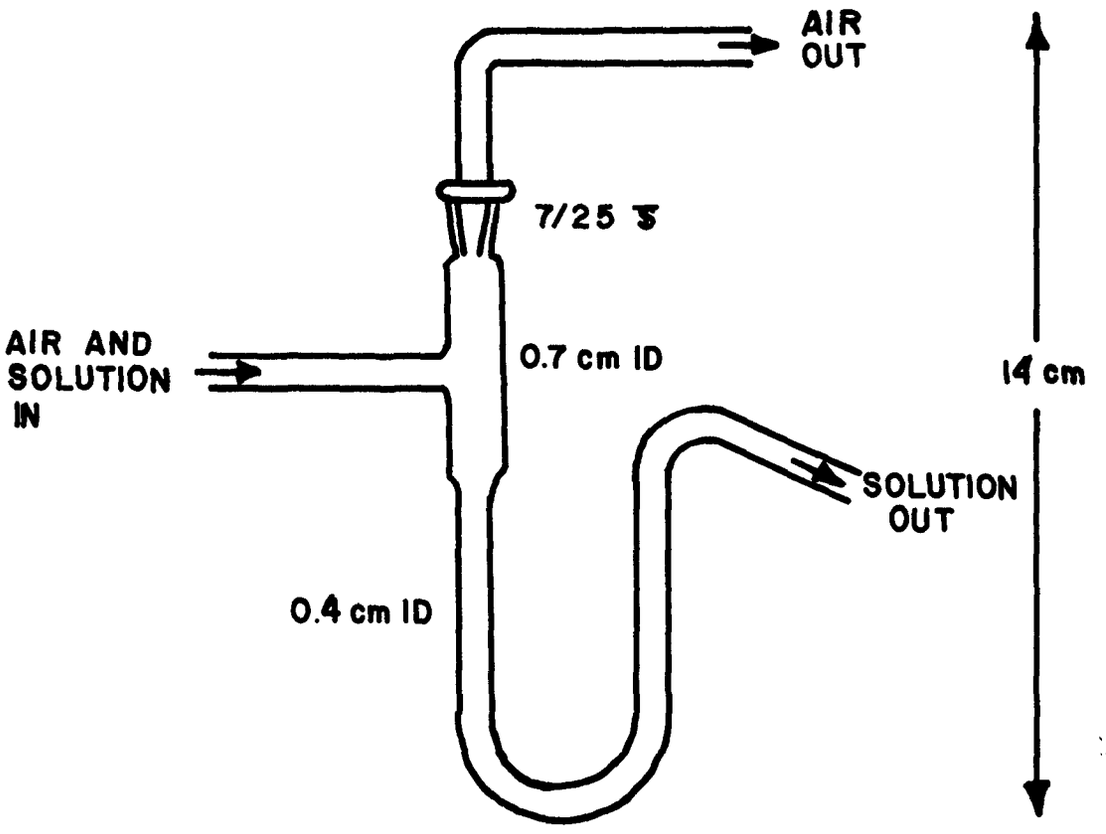

FIGURE 1. VAPOR LIQUID SEPARATOR

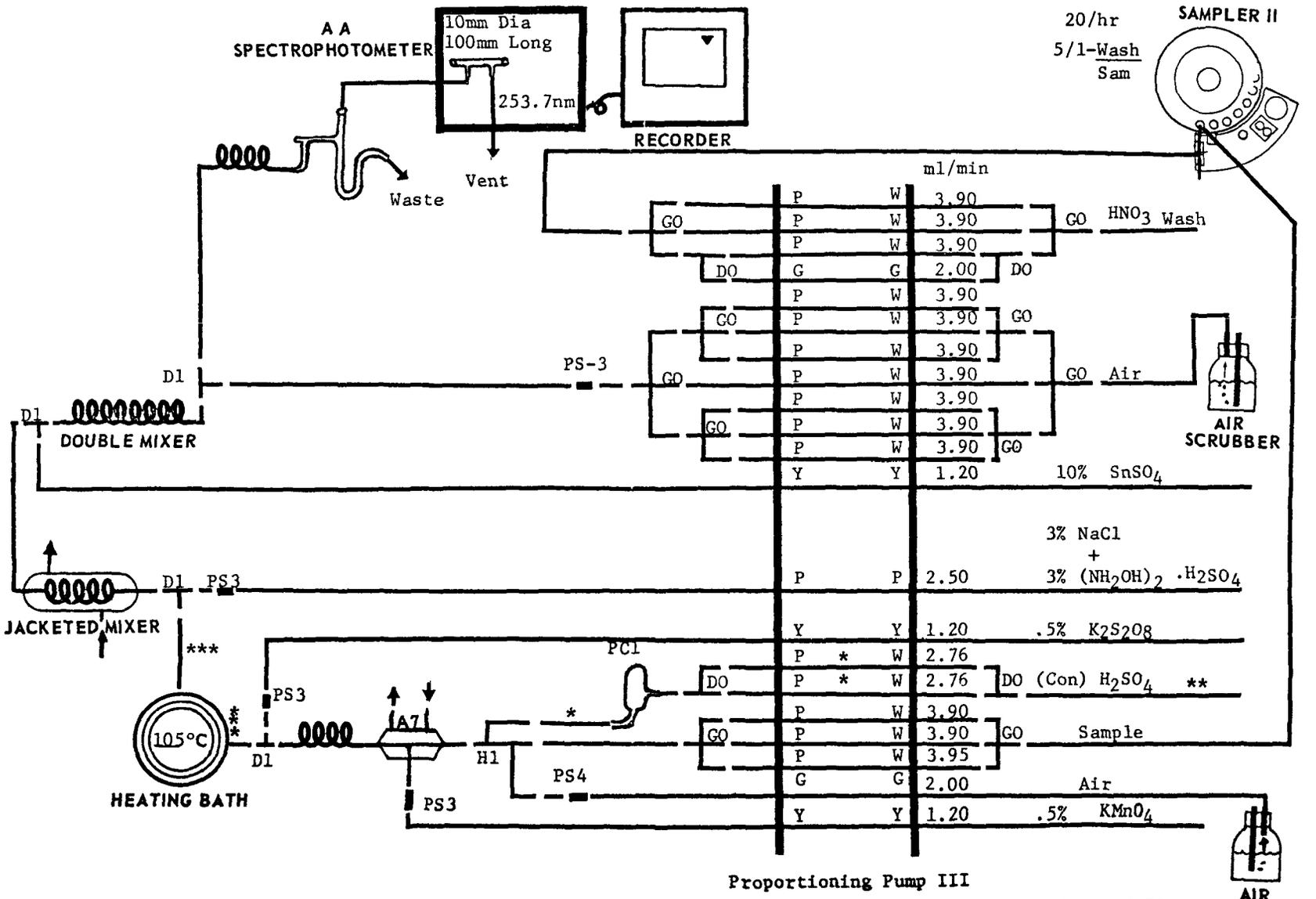

FIGURE 2 MERCURY MANIFOLD AA-I

working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot.

7. Calibration

7.1 Transfer 0, 0.5, 1.0, 2.0, 5.0 and 10 ml aliquots of the working mercury solution (6.7) containing 0 to 1.0 ug of mercury to a series of 300 ml **BOD** bottles. Add enough distilled water to each bottle to make a total volume of 10 ml. Add 5 ml of aqua regia (6.1) and heat 2 minutes in a water bath at 95°C. Allow the sample to cool and add 50 ml distilled water and 15 ml of $KMnO_4$ solution (6.5) to each bottle and return to the water bath for 30 minutes. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Add 50 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate solution (6.3) and immediately attach the bottle to the aeration apparatus. At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to rate of 1 liter per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the recorder pen levels off, approximately 1 minute, open the bypass value and continue the aeration until the absorbance returns to its minimum value (See Note 5). Close the bypass value, remove the fritted tubing from the **BOD** bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus micrograms of mercury.

NOTE 5: Because of the toxic nature of mercury vapor 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:

a) equal volumes of 0.1 N $KMnO_4$ and 10% H_2SO_4

b) 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will absorb mercury vapor is also available from Barnebey and Cheney, E. 8th Ave., and North Cassidy St., Columbus, Ohio 43219, Cat. #580–13 or #580–22.

8. Procedure

8.1 Weigh triplicate 0.2 g portions of dry sample and place in bottom of a **BOD** bottle. Add 5 ml of distilled water and 5 ml of aqua regia (6.1). Heat 2 minutes in a water bath at 95°C. Cool, add 50 ml distilled water and 15 ml potassium permanganate solution (6.5) to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 ml of sodium chloride-hydroxylamine sulfate (6.4) to reduce the excess permanganate. Add 55 ml of distilled water. Treating each bottle individually, add 5 ml of stannous sulfate (6.3) and immediately attach the bottle to the aeration apparatus. Continue as described under (7.1).

8.2 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. 5 ml of saturated $KMnO_4$ solution is added and the bottle covered with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lbs. for 15 minutes. Cool, make up to a volume of 100 ml with distilled water and add 6 ml of sodium chloride-

hydroxylamine sulfate solution (6.4) to reduce the excess permanganate. Purge the dead air space and continue as described under (7.1).

9. Calculation
   9.1 Measure the peak height of the unknown from the chart and read the mercury value from the standard curve.
   9.2 Calculate the mercury concentration in the sample by the formula:

$$ug\,Hg/g = \frac{ug\,Hg \text{ in the aliquot}}{\text{wt of the aliquot in gms}}$$

   9.3 Report mercury concentrations as follows: Below 0.1 *ug*/gm, <0.1; between 0.1 and 1 *ug*/gm, to the nearest 0.01 *ug*; between 1 and 10 *ug*/gm, to nearest 0.1 *ug*; above 10 *ug*/gm, to nearest *ug*.
10. Precision and Accuracy
   10.1 The following standard deviations on replicate sediment samples were recorded at the indicated levels; 0.29 *ug*/g ±0.02 and 0.82 *ug*/g ±0.03. Recovery of mercury at these levels, added as methyl mercuric chloride, was 97% and 94%, respectively.

Bibliography

1. Bishop, J. N., "Mercury in Sediments", Ontario Water Resources Comm., Toronto, Ontario, Canada, 1971.
2. Salma, M., private communication, EPA Cal/Nev Basin Office, Almeda, California.

NICKEL
Method 249.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 0.3–5 mg/1 using a wavelength of 232.0 nm
Sensitivity: 0.15 mg/1
Detection Limit: 0.04 mg/1

Preparation of Standard Solution

1. Stock Solution: Dissolve 4.953 g of nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade) in deionized distilled water. Add 10 ml of conc. nitric acid and dilute to 1 liter with deionized distilled water. 1 ml = 1 mg Ni (1000 mg/1).
2. Prepare dilutions of the stock nickel solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.4 of the Atomic Absorption Methods section of this manual have been found to be satisfactory.

Instrumental Parameters (General)

1. Nickel hollow cathode lamp
2. Wavelength: 232.0 nm
3, Fuel: Acetylene
4. Oxidant: Air
5. Type of Flame: Oxidizing

Analysis Procedure

1. For analysis procedure and calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

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Interferences

1. The 352.4 nm wavelength is less susceptible to spectral interference and may be used. The calibration curve is more linear at this wavelength; however, there is some loss of sensitivity.

Notes

1. For levels of nickel below 100 ug/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace technique, Method 249.2, is recommended.
2. Data to be entered into **STORET** must be reported as ug/1.
3. The heptoxime method may also be used (Standard Methods, 14th Edition, p 232).

Precision and Accuracy

1. In a single laboratory (EMSL), using a mixed industrial-domestic waste effluent at concentrations of 0.20, 1.0 and 5.0 mg Ni/1, the standard deviations were ±0.011, ±0.02 and ±0.04, respectively. Recoveries at these levels were 100%, 97% and 93%, respectively.

NICKEL

Method 249.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01067
Dissolved 01065
Suspended 01066

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 1 *ug/l*

Preparation of Standard Solution

1. Stock solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–900°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 232.0 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 *ul* injection, continuous flow purge gas and pyrolytic

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graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

2. The use of background correction is recommended.
3. Nitrogen may also be used as the purge gas.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
6. Data to be entered into STORET must be reported as *ug/1*.

Precision and Accuracy

1. Precision and accuracy data are not available at this time.

SELENIUM

Method 270.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

Optimum Concentration Range: 5–100 *ug/l*
Detection Limit: 2 *ug/l*

Preparation of Standard Solution

1. Stock Selenium Solution: Dissolve 0.3453 g of selenous acid (actual assay 94.6% H_2SeO_3) in deionized distilled water and make up to 200 ml. 1 ml = 1 mg Se (1000 mg/l).
2. Nickel Nitrate Solution, 5%: Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ in deionized distilled water and make up to 100 ml.
3. Nickel Nitrate Solution, 1%: Dilute 20 ml of the 5% nickel nitrate to 100 ml with deionized distilled water.
4. Working Selenium Solution: 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. HNO_3, 2 ml of 30% H_2O_2 and 2 ml of the 5% nickel nitrate solution. Dilute to 100 ml with deionized distilled water.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Transfer 100 ml of well-mixed sample to a 250 ml Griffin beaker, add 2 ml of 30% H_2O_2 and sufficient conc. HNO_3 to result in an acid concentration of 1%(v/v). Heat for 1 hour at 95°C or until the volume is slightly less than 50 ml.
2. Cool and bring back to 50 ml with deionized distilled water.
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 deionized distilled water. The sample is now ready for injection into the furnace. NOTE: If solubilization or digestion is not required adjust the HNO_3 concentration of the sample to 1% (v/v) and add 2 ml of 30% H_2O_2 and 2 ml of 5% nickel nitrate to each 100 ml of sample. The volume of the calibration standard should be adjusted with deionized distilled water to match the volume change of the sample.

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Instrument Parameters

1. Drying time and temperature: 30 sec @ 125°C
2. Charring time and temperature: 30 sec @ 1200°C
3. Atomizing time and temperature: 10 sec @ 2700°C
4. Purge Gas Atmosphere: Argon
5. Wavelength: 196.0 nm.
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. The use of background correction is recommended.
3. Selenium analysis suffers interference from chlorides ($>$ 800 mg/1) and sulfate ($>$ 200 mg/1). For the analysis of industrial effluents and samples with concentrations of sulfate from 200 to 2000 mg/1, both samples and standards should be prepared to contain 1% nickel.
4. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
5. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
6. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
7. Data to entered into STORET must be reported as *ug*/1.

Precision and Accuracy

1. Using a sewage treatment plant effluent containing $<$2 *ug*/1 and spiked with a concentration of 20 *ug*/1, a recovery of 99% was obtained.
2. Using a series of industrial waste effluents spiked at a 50 *ug*/1 level, recoveries ranged from 94 to 112%.
3. Using a 0.1% nickel nitrate solution as a synthetic matrix with selenium concentrations of 5, 10, 20, 40, 50, and 100 *ug*/1, relative standard deviations of 14.2, 11.6, 9.3, 7.2, 6.4 and 4.1%, respectively, were obtained at the 95% confidence level.

4. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 5, 10, and 20 *ug* Se/1, the standard deviations were ±0.6, ±0.4, and ±0.5, respectively. Recoveries at these levels were 92%, 98%, and 100%, respectively.

Reference:

"Determining Selenium in Water, Wastewater, Sediment and Sludge By Flameless Atomic Absorption Spectroscopy", Martin, T. D., Kopp, J. F. and Ediger, R. D. Atomic Absorption Newsletter 14, 109 (1975).

SELENIUM

Method 270.3 (Atomic Absorption, gaseous hydride)

STORET NO. Total 01147
Dissolved 01145
Suspended 01146

1. Scope and Application
   1.1 The gaseous hydride method determines inorganic selenium when present in concentrations at or above 2 *ug*/1. The method is applicable to drinking water and most fresh and saline waters, in the absence of high concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel and silver.
2. Summary of Method
   2.1 Selenium in the sample is reduced from the +6 oxidation state to the +4 oxidation state by the addition of $SnCl_2$. Zinc is added to the acidified sample, producing hydrogen and converting the selenium to the hydride, SeH_2. The gaseous selenium hydride is swept into an argon-hydrogen flame of an atomic absorption spectrophotometer. The working range of the method is 2–20 *ug*/1 using the 196.0 nm wavelength.
3. Comments
   3.1 In analyzing drinking water and most surface and ground waters, interferences are rarely encountered. Industrial waste samples should be spiked with a known amount of selenium to establish adequate recovery.
   3.2 Organic forms of selenium must be converted to an inorganic form and organic matter must be oxidized before beginning the analysis. The oxidation procedure given in method 206.5 (Standard Methods, 14*th* Ed. 404B, p 285, Procedure 4.1) should be used.
   3.3 For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.
   3.4 For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
   3.5 Data to be entered into STORET must be reported as *ug*/1.
4. Precision and Accuracy
   4.1 Ten replicate solutions of selenium oxide at the 5, 10 and 15 *ug*/1 level were analyzed by a single laboratory. Standard deviations at these levels were ±0.6, ±1.1 and ±2.9 with recoveries of 100, 100 and 101%. (Caldwell, J. S., Lishka, R. J., and McFarren, E. F., "Evaluation of a Low-Cost Arsenic and Selenium Determination at Microgram per Liter Levels", JAWWA, vol 65, p. 731, Nov. 1973.)

Approved for NPDES and SDWA
Issued 1974

5. References

5.1 Except for the perchloric acid step, the procedure to be used for this determination is found in:

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 159, Method 301A(VII), (1975)

SILVER

Method 272.2 (Atomic Absorption, furnace technique)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 1–25 *ug/l*
Detection Limit: 0.2 *ug/l*

Preparation of Standard Solution

1. Stock Solution: Prepare as described under "direct aspiration method".
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These solutions are also to be used for "standard additions".
3. The calibration standard should be diluted to contain 0.5% (v/v) HNO_3.

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. Prepare as described under "direct aspiration method". Sample solutions for analysis should contain 0.5% (v/v) HNO_3.

Instrument Parameters (General)

1. Drying Time and Temp: 30 sec–125°C.
2. Ashing Time and Temp: 30 sec–400°C.
3. Atomizing Time and Temp: 10 sec–2700°C.
4. Purge Gas Atmosphere: Argon
5. Wavelength: 328.1 nm
6. Other operating parameters should be set as specified by the particular instrument manufacturer.

Analysis Procedure

1. For the analysis procedure and the calculation, see "Furnace Procedure" part 9.3 of the Atomic Absorption Methods section of this manual.

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Notes

1. The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 ul injection, continuous flow purge gas and non-pyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.
2. Background correction may be required if the sample contains high dissolved solids.
3. The use of halide acids should be avoided.
4. If adsorption to container walls or formation of AgCl is suspected, see NOTE 3 under the Direct Aspiration Method 272.1.
5. For every sample matrix analyzed, verification is necessary to determine that method of standard addition is not required (see part 5.2.1 of the Atomic Absorption Methods section of this manual).
6. For quality control requirements and optional recommendations for use in drinking water analyses, see part 10 of the Atomic Absorption Methods section of this manual.
7. If method of standard addition is required, follow the procedure given earlier in part 8.5 of the Atomic Absorption Methods section of this manual.
8. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy:

1. In a single laboratory (EMSL), using Cincinnati, Ohio tap water spiked at concentrations of 25, 50, and 75 ug Ag/1, the standard deviations were ±0.4, ±0.7, and ±0.9, respectively. Recoveries at these levels were 94%, 100% and 104%, respectively.

SILVER

Method 272.1 (Atomic Absorption, direct aspiration)

STORET NO. Total 01077
Dissolved 01075
Suspended 01076

Optimum Concentration Range: 0.1–4 mg/1 using a wavelength of 328.1 nm
Sensitivity: 0.06 mg/1
Detection Limit: 0.01 mg/l

Preparation of Standard Solution

1. Stock Solution: Dissolve 1.575 g of $AgNO_3$ (analytical reagent grade) in deionized distilled water, add 10 ml conc. HNO_3 and make up to 1 liter. 1 ml = 1 mg Ag (1000 mg/1).
2. Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using nitric acid and at the same concentration as will result in the sample to be analyzed either directly or after processing.
3. Iodine Solution, 1 N: Dissolve 20 grams of potassium iodide, KI (analytical reagent grade) in 50 ml of deionized distilled water, add 12.7 grams of iodine, I_2 (analytical reagent grade) and dilute to 100 ml. Store in a brown bottle.
4. Cyanogen Iodide (CNI) Solution: To 50 ml of deionized distilled water add 4.0 ml conc. NH_4OH, 6.5 grams KCN, and 5.0 ml of 1.0 N I_2 solution. Mix and dilute to 100 ml with deionized distilled water. Fresh solution should be prepared every two weeks.[1]

Sample Preservation

1. For sample handling and preservation, see part 4.1 of the Atomic Absorption Methods section of this manual.

Sample Preparation

1. The procedures for preparation of the sample as given in parts 4.1.1 thru 4.1.3 of the Atomic Absorption Methods section of this manual have been found to be satisfactory; however, the residue must be taken up in dilute nitric acid rather than hydrochloric to prevent precipitation of AgCl.

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Technical revision 1978

Instrumental Parameters (General)

1. Silver hollow cathode lamp
2. Wavelength: 328.1 nm
3. Fuel: Acetylene
4. Oxidant: Air
5. Type of flame: Oxidizing

Analysis Procedure

1. For the analysis procedure and the calculation, see "Direct Aspiration", part 9.1 of the Atomic Absorption Methods section of this manual.

Notes

1. For levels of silver below 30 ug/1, either the Special Extraction Procedure, given in part 9.2 of the Atomic Absorption Methods section or the furnace procedure, Method 272.2, is recommended.
2. Silver nitrate standards are light sensitive. Dilutions of the stock should be discarded after use as concentrations below 10 mg/1 are not stable over long periods of time.
3. If absorption to container walls or the formation of AgCl is suspected, make the sample basic using conc. NH_4OH and add 1 ml of (CNI) solution per 100 ml of sample. Mix the sample and allow to stand for 1 hour before proceeding with the analysis.[1]
4. The 338.2 nm wavelength may also be used. This has a relative sensitivity of 2.
5. Data to be entered into STORET must be reported as ug/1.

Precision and Accuracy

1. In a round-robin study reported by Standard Methods, a synthetic sample containing 50 ug Ag/1 was analyzed by 50 laboratories with a reported standard deviation of ±8.8 and a relative error 10.6%.

References

1. "The Use of Cyanogen Iodide (CNI) as a Stabilizing Agent for Silver in Photographic Processing Effluent Sample", Owerbach, Daniel, Photographic Technology Division, Eastman Kodak Company, Rochester, N.Y. 14650.
2. Standard Methods for Examination of Water and Wastewater, 14th Edition, p. 148, Method 301A.

APPENDIX III

METHODS FOR BENZIDINE, CHLORINATED ORGANIC COMPOUNDS, PENTACHLOROPHENOL AND PESTICIDES IN WATER AND WASTEWATER

METHODS FOR BENZIDINE, CHLORINATED ORGANIC COMPOUNDS, PENTACHLOROPHENOL AND PESTICIDES IN WATER AND WASTEWATER

INTERIM
Pending Issuance of
Methods for Organic Analysis
of Water and Wastes

U.S. ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
CINCINNATI, OHIO 42568

September 1978

FOREWORD

This collection of methods for the determination of benzidine, chlorinated organic compounds, pentachlorophenol and pesticides has been assembled by the staff of the Environmental Monitoring and Support Laboratory - Cincinnati (EMSL-Cinti.) for use by the NPDES Permits Program.

These methods are as referenced in the Federal Register of December 1, 1976 and are being provided only for the interim period until the manual "Methods for Organic Analysis of Water and Wastes" becomes available.

Dwight G. Ballinger, Director
Environmental Monitoring and Support Laboratory - Cincinnati

DISCLAIMER

The mention of trade names or commercial products in this manual is for illustration purposes, and does not constitute endorsement or recommendatior by the U. S. Environmental Protection Agency.

TABLE OF CONTENTS

PAGE REFERENCES

F.R.#	Parameter	EPA This Manual	14th ed. Std. Methods	ASTM (1975)	USGS*	STORET NUMBER
9	Benzidine	1	--	--	--	39120
14	Chlorinated organic compounds:					
	Benzylchloride	130	--	--	--	--
	Carbon tetrachloride	130	--	--	--	32102
	Chlorobenzene	130	--	--	--	34301
	Chloroform	130	--	--	--	32160
	Epichlorohydrin	130	--	--	--	--
	Heptachloro epoxide	--	555	529	30	39420
	Methylene chloride	130	--	--	--	34423
	PCB-1016	43	--	--	--	34671
	PCB-1221	43	--	--	--	39488
	PCB-1232	43	--	--	--	39492
	PCB-1242	43	--	--	--	39496
	PCB-1248	43	--	--	--	39500
	PCB-1254	43	--	--	--	39504
	PCB-1260	43	--	--	--	39508
	1,1,2,2-Tetrachloroethane	130	--	--	--	--
	Tetrachloroethylene	130	--	--	--	34475
	1,2,4-Trichlorobenzene	130	--	--	--	--
	1,1,2-Trichloroethane	130	--	--	--	--
94	Pentachlorophenol	140	--	--	--	39032
95	Pesticides					
	Aldrin	7	555	529	30	39330
	Ametryn	83	--	--	--	--
	Aminocarb	94	--	--	--	--
	Atraton	83	--	--	--	--
	Atrazine	83	--	--	--	39033
	Azinphos methyl	25	--	--	--	--
	Barban	104	--	--	--	--
	BHC	7	555	529	--	--
	Captan	7	555	--	--	39640
	Carbaryl	94	--	--	--	39750
	Carbophenothion	--	--	--	30	--
	Chlordane	7	555	529	--	39350
	Chlorpropham	104	--	--	--	--
	2,4-D	115	--	--	35	--

F.R.#	Parameter	EPA This Manual	14th ed. Std. Methods	ASTM (1975)	USGS*	STORET NUMBER
	DDD	7	555	529	30	39360
	DDE	7	555	529	30	39365
	DDT	7	555	529	30	39370
	Demeton-O	25	--	--	--	39560
	Diazinon	25	--	--	30	39570
	Dicamba	115	--	--	--	
	Dichlorofenthion	--	--	--	30	--
	Dichloran	7	555	--	-	--
	Dicofol	--	--	529	-	39780
	Dieldrin	7	--	--	30	--
	Dioxathion	--	--	--	30	--
	Disulfoton	25	--	--	-	39010
	Diuron	104	--	--	--	39650
	Endosulfan	7	555	529	--	39388
	Edrin	7	555	529	30	39390
	Ethion	--	--	--	30	39398
	Fenuron	104	--	--	--	--
	Fenuron - TCA	104	--	--	--	--
	Heptachlor	7	555	529	30	39410
	Isodrin	--	--	--	30	39430
	Lindane	7	555	529	30	39782
	Linuron	104	--	--	--	--
	Malathion	25	555	--	30	39530
	Methiocarb	94	--	--	--	--
	Methoxychlor	7	555	529	30	39489
	Mexacarbate	94	--	--	--	--
	Mirex	7	555	--	--	39755
	Monuron	104	--	--	--	--
	Monuron-TCA	104	--	--	--	--
	Neburon	104	--	--	--	--
	Parathion methyl	25	555	--	30	39600
	Parathion ethyl	25	555	--	--	39540
	PCNB	7	555	--	--	39029
	Perthane	--	--	529	--	39034
	Prometon	83	--	--	--	39056
	Prometryn	83	--	--	--	39057
	Propazine	83	--	--	--	39024
	Propham	104	--	--	--	39052
	Proporur	94	--	--	--	--
	Secbumeton	83	--	--	--	--
	Siduron	104	--	--	--	--
	Silvex	115	--	--	35	39760
	Simazine	83	--	--	--	39055
	Strobane	7	555	529	--	--
	Swep	104	--	--	--	--
	2,4,5-T	115	--	--	35	--
	Terbuthylazine	83	--	--	--	--

F.R.#	Parameter	EPA This Manual	14th ed. Std. Methods	ASTM (1975)	USGS*	STORET NUMBER
	Toxaphene	7	555	529	30	39400
	Trifluraline	7	--	--	--	39030

*Goerlitz, D. & Brown, E. "Methods for Analysis of Organic Substances in Water," U.S. Geological Survey Techniques of Water-Resources Inv. Book 5, Ch. A3 (1972).

METHOD FOR BENZIDINE AND ITS SALTS IN WASTEWATERS

1. Scope and Application

   1.1 This method covers the determination for benzidine and its salts in water and wastewaters. The method can be modified to apply also to the determination of closely related materials as described under Interferences (4.2).

   1.2 The salts of benzidine, such as benzidine sulfate, are measured and reported as benzidine, STORET NO. 39120.

   1.3 The method detection limit is 0.2 µg/l when analyzing 1 liter of sample.

2. Summary

   2.1 The water sample is made basic and the benzidine is extracted with ethyl acetate. Cleanup is accomplished by extracting the benzidine from the ethyl acetate with hydrochloric acid. Chloramine-T is added to the acid solution to oxidize the benzidine. The yellow oxidation product is extracted with ethyl acetate and measured with a scanning spectrophotometer. The spectrum from 510 nm to 370 nm is used for qualitative identification.

3. Hazards

   3.1 Benzidine is a known carcinogen. All manipulations of this method should be carried out in a hood with protection

provided for the hands and arms of the analyst. Consult OSHA regulations (1) before working with benzidine.

4. Interferences

4.1 The multiple extractions effectively limit the interferences to organic bases. The oxidation with Chloramine-T to form a yellow product is very selective and has been described in detail (2,3). The use of the absorption spectrum for the identification of benzidine results in a highly specific procedure.

4.2 Some compounds having a structure very similar to benzidine will interfere with the quantification, if present. Examples of these interferring compounds are dichlorobenzidine, o-tolidine, and dianisidine.

4.3 A general yellow background color in the extract will limit the cell pathlength that can be employed and thus limit the sensitivity of the method.

5. Apparatus and Materials

5.1 Spectrophotometer-visible, scanning (510-370 nm).

5.2 Separatory Funnels - 125 ml, 250 ml, 2000 ml.

5.3 Cells - 1 to 5 cm pathlength, 20 ml volume maximum.

6. Reagents, Solvents and Standards

6.1 Ethyl acetate

6.2 Hydrochloric acid (1 N) - Add 83 ml conc. hydrochloric acid to water and dilute to one liter.

6.3 Chloramine-T - 10% solution. Prepare fresh daily by dissolving 1.0g Chloramine-T in 10 ml distilled water.

6.4 Stock standard (0.2 µg/µl) - Dissolve 100.0 mg purified benzidine in about 30 ml 1 N HCl. Dilute to 500 ml with water.

7. Preparation of Calibration Curve

7.1 To a series of 125-ml separatory funnels, add 45 ml of hydrochloric acid and 10 ml of ethyl acetate. Shake for one minute to saturate the acid layers. Discard the solvent layers. Dose the series with volumes from 1.0 to 20.0 µl of stock standard, using syringes.

7.2 Treat standards according to the Procedure beginning with 8.5.

8. Quality Control

8.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

8.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

9. Procedure

9.1 Adjust the sample pH to 8.5 to 9.0 with dilute NaOH or HCl.

9.2 Transfer 1 liter of sample to a 2000-ml separatory funnel. Add 150 ml ethyl acetate and shake for two minutes. Allow the layers to separate, then drain the water layer into a

second 2-liter separatory funnel. Drain the solvent layer into a 250-ml separatory funnel.

9.3 Repeat the extraction of the water layer twice more with 50-ml portions of ethyl acetate. Combine all solvent layers, then discard the water layer.

9.4 Extract the solvent layer three times with 15-ml portions of hydrochloric acid by shaking 2 minutes and allowing the phases to separate. Combine the acid layers in a glass stoppered container for cold storage until time is available for analysis, or transfer the layers directly into a 125-ml separatory funnel.

9.5 Prepare the spectrophotometer so it is warmed and ready to use. The remaining steps of the procedure must be performed rapidly on one sample at a time.

9.6 To the hydrochloric acid solution in a 125 ml separatory funnel, add 1.0 ml chloramine-T solution and mix. Add 25.0-ml ethyl acetate with a pipet and shake for two minutes. Allow the layers to separate, then discard the aqueous phase.

9.7 Filter the solvent layer through coarse filter paper and fill a 5-cm cell with the filtrate.

9.8 Scan the solvent from 510 nm to 370 nm. Ethyl acetate is used for a blank with double beam instruments. Shorter pathlength cells should be used in cases where absorbance exceeds 0.8.

10. Calculation of Results

10.1 Benzidine is identified by its absorbance maximum at 436 nm. Dichlorobenzidine gives similar response but has its absorbance maximum at 445 nm.

10.2 Construct a baseline from the absorbance minimum at about 470 nm to the minimum at 390 nm (or 420 nm minimum for samples with a high background). Record the absorbance ofthe peak maximum and the absorbance of the constructed baseline at the 436 nm. Treat samples and standards in the same fashion.

10.3 Using the net absorbance values, prepare a calibration plot from the standards. Determine the total micrograms in each sample from this plot.

10.4 Divide the total micrograms by the sample volume, in liters, to determine µg/l. Correct results for cell pathlength if necessary.

11. Reporting Results

11.1 Report results in micrograms per liter as benzidine without correction for recovery data. When duplicate and spike samples are analyzed all data obtained should be reported.

12. Accuracy and Precision

12.1 When 1 liter samples of river water were dosed with 1.80 µg of benzidine, an average of 1.24 µg was recovered. The standard deviation was 0.092 µg/l (n=8).

REFERENCES:

1. Federal Register, Volume 39, Page 3779, Paragraph 1910.93; (January 29, 1974).

2. Glassman, J. M., and Meigs, J. W., "Benzidine (4,4'-Diaminobiphenyl) and Substituted Benzidines", Arch. Industr. Hyg., 4, 519, (1951).

3. Butt, L. T. and Strafford, N., "Papilloma of the Bladder in the Chemical Industry. Anlaytical Methods for the Determination of Benzidine and B-Naphtylamine, Recommended by A.B.C.M. Sub-Committee", J. Appl. Chem., 6, 525 (1956).

METHOD FOR CHLORINATED HYDROCARBONS IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various organochlorine pesticides and heptachlor epoxide in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Aldrin	39330
BHC	----
Captan	39640
Chlordane	39350
DDD	39360
DDE	39365
DDT	39370
Dichloran	----
Dieldrin	39380
Endosulfan	39388
Endrin	39390
Heptachlor	39410
Lindane	39782
Methoxychlor	39480
Mirex	39755
PCNB	39029
Strobane	----
Toxaphene	39400
Trifluralin	39030

1.3 The following chlorinated organic compound may be determined individually by this method:

Compound	Storet No.
Heptachlor epoxide	----

2. Summary

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and/or the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of column chromatography and liquid-liquid partition, methods for elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or electrolytic conductivity gas chromatography. Results are reported in micrograms per liter.

2.2 Confirmation of the identity of the compounds should be made by GC-MS when a new or undefined sample type is being analyzed and the concentration is adequate for such determination.

2.3 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of gas chromatograms.

All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organochlorine pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organochlorine pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Polychlorinated Biphenyls (PCBs) - Special attention is called to industrial plasticizers and hydraulic fluids such as the PCBs, which are a potential source of interference in pesticide analysis. The presence of PCBs is indicated by a large number of partially resolved or unresolved peaks which may occur throughout the entire chromatogram. Particularly severe PCB interference will require special separation procedures (1, 2).

3.4 Phthalate Esters - These compounds, widely used as plasticizers, respond to the electron capture detector and are a source of interference in the determination of organochlorine pesticides using this detector. Water leaches these materials from plastics, such as polyethylene bottles and tygon tubing.

The presence of phthalate esters is implicated in samples that respond to electron capture but not to the microcoulometric or electrolytic conductivity halogen detectors or to the flame photometric detector.

3.5 Organophosphorus Pesticides - A number of organophosphorus pesticides, such as those containing a nitro group, e.g., parathion, also respond to the electron capture detector and may interfere with the determination of the organochlorine pesticides. Such compounds can be identified by their response to the flame photometric detector (3).

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel-63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long X 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas-Chrom-Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 OV-1, 3%

4.4.4.2 OV-210, 5%

4.4.4.3 OV-17, 1.5% plus QF-1 or OV-210, 1.95%

4.4.4.4 QF-1, 6% plus SE-30, 4%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three-ball (macro) and two-ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250-ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540- 9011).

4.7 Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 μl.

4.9 Separatory funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Graduated cylinders - 100 and 250 ml.

4.12 Florisil - PR Grade (60-100 mesh); purchase activated at 1250^{o}F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130^{o}C in foil-covered glass container. Determine lauric-acid value (See Appendix II).

5. Reagents, Solvents, and Standards

5.1 Sodium Chloride - (ACS) Saturated solution in distilled water

(pre-rinse NaCl with hexane).

5.2 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400 C for 4 hrs.).

5.4 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.5 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.6 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - nanograde, redistill in glass if necessary.

5.7 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\leq$ 0.06 ng is injected for electron capture detection and $\geq$ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard

pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organochlorine pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (4) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 The sample size taken for analysis is dependent on the type of sample and the sensitivity required for the purpose at hand. Background information on the pesticide levels previously detected at a given sampling site will assist in determining the sample size required, as well as the final volume to which the extract needs to be concentrated. A 1-liter sample is usually taken for drinking water and ambient water analysis to provide a detection limit of 0.050to 0.100 µg/l. One-hundred milliliters is usually adequate to provide a detection limit of 1 µg/l for industrial effluents.

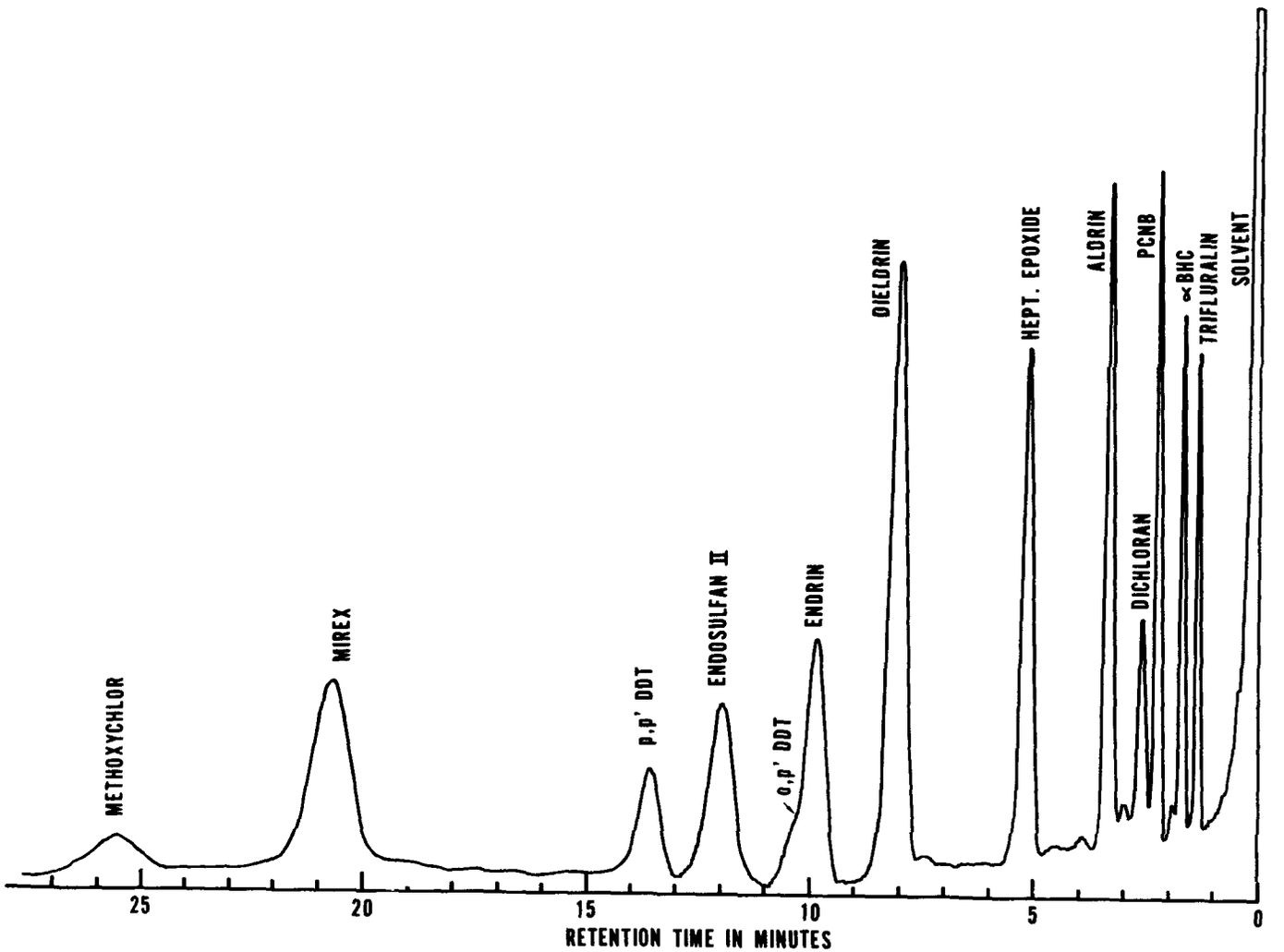

Figure 1. Column Packing: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

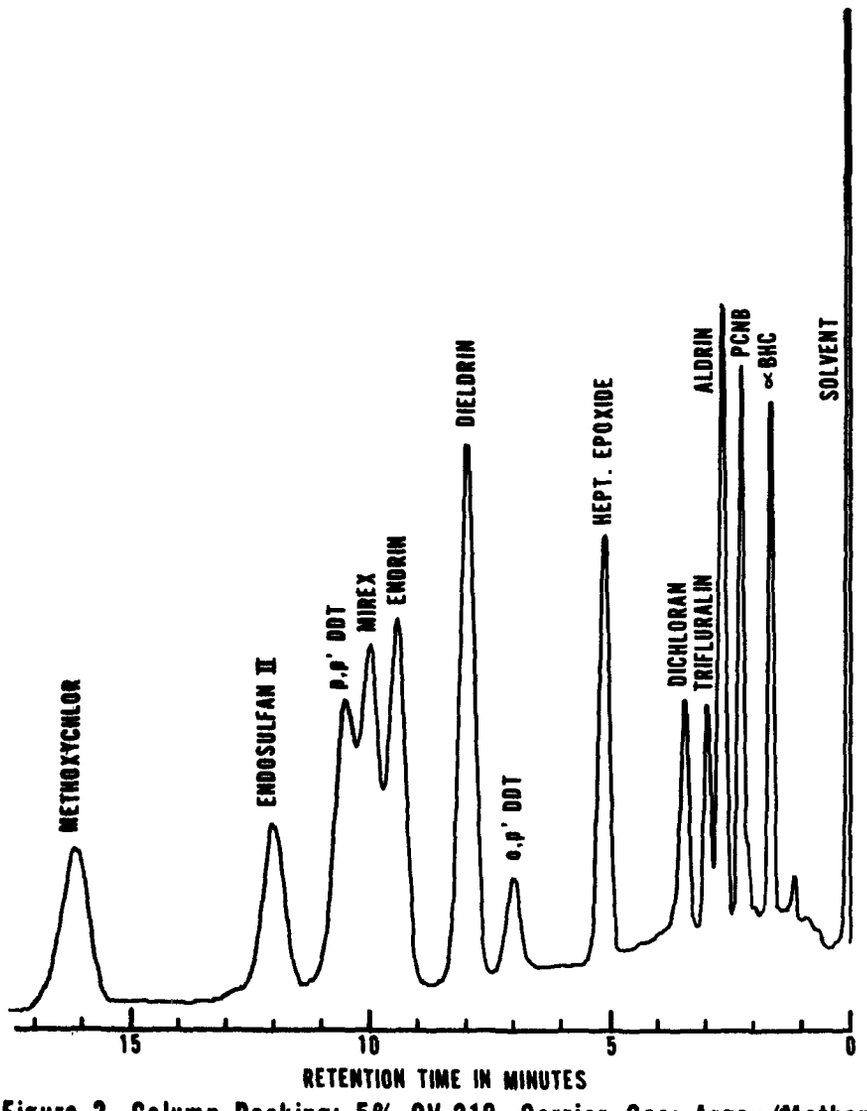

Figure 2. Column Packing: 5% OV-210, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

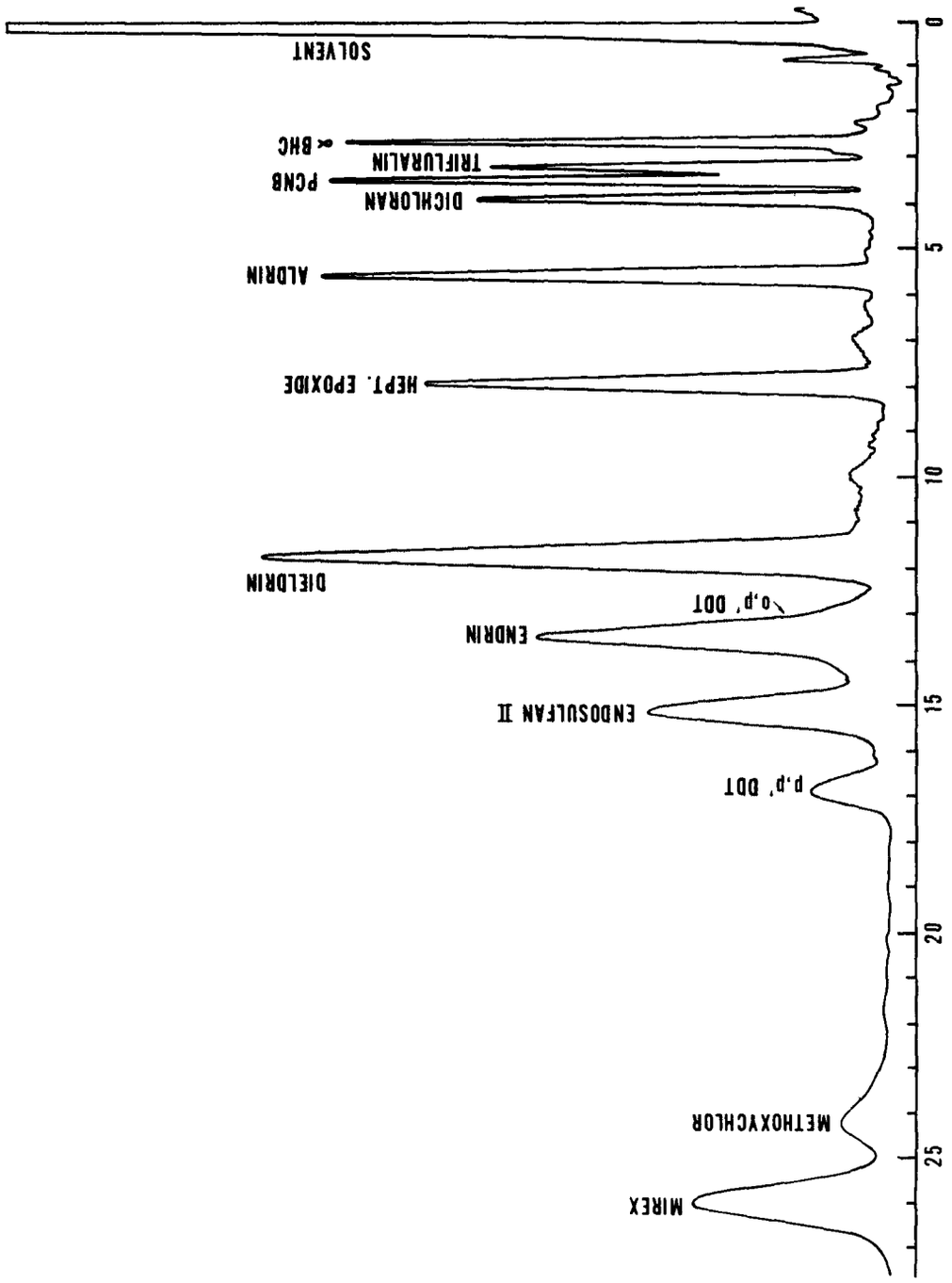

Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Argon/Methane at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

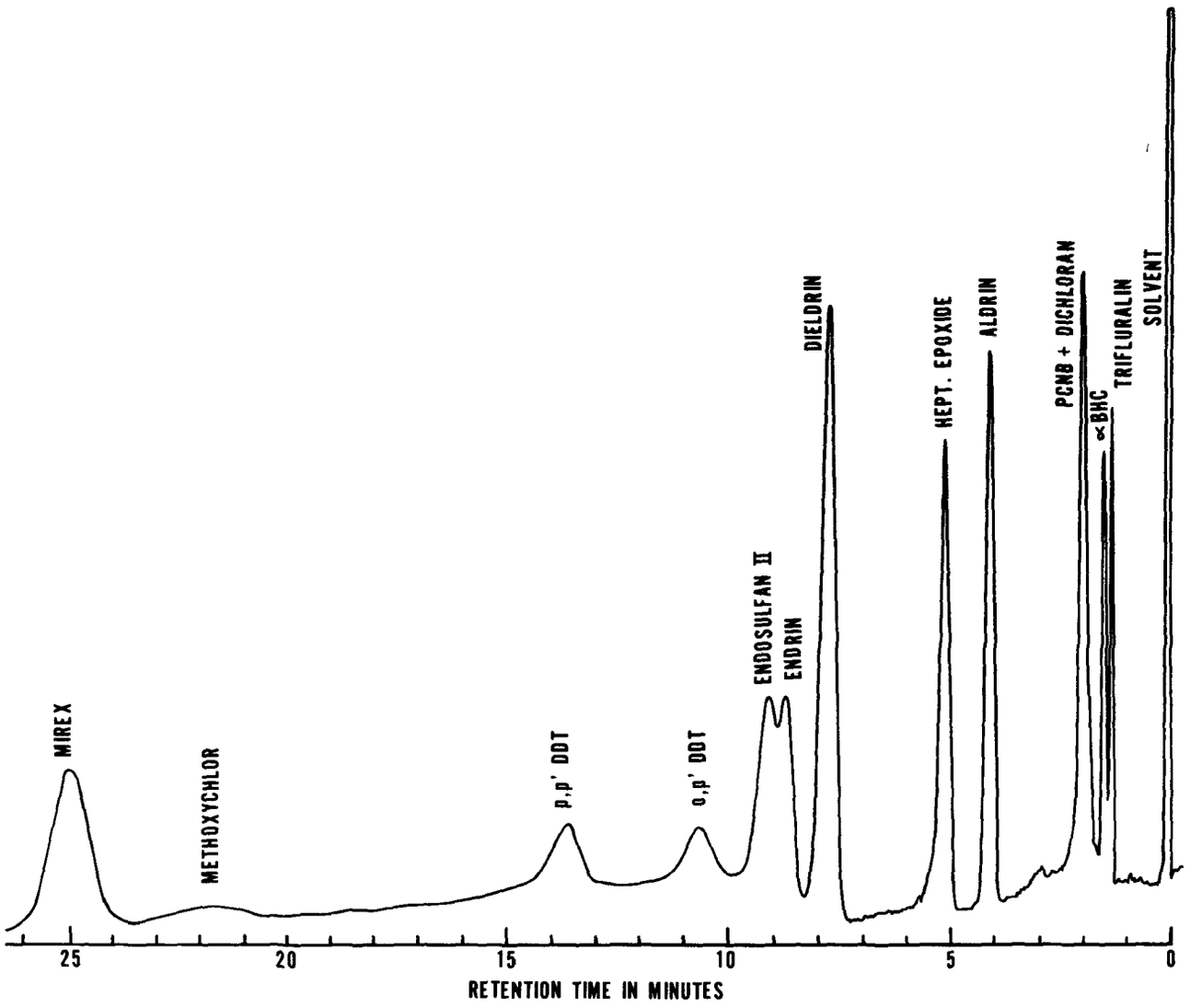

Figure 4. Column Packing: 3% OV-1, Carrier Gas: Argon/Methane at 70 ml/min, Column Temperature: 180 C, Detector: Electron Capture.

Table 1
RETENTION RATIOS OF VARIOUS ORGANOCHLORINE PESTICIDES RELATIVE TO ALDRIN

Liquid Phase[1]	1.5% OV-17 + 1.95% QF-1[2]	5% OV-210	3% OV-1	6% QF-1 + 4% SE-30
Column Temp.	200 C	180 C	180 C	200 C
Argon/Methane Carrier Flow	60 ml/min	70 ml/min	70 ml/min	60 ml/min
Pesticide	RR	RR	RR	RR
Trifluralin	0.39	1.11	0.33	0.57
∝-BHC	0.54	0.64	0.35	0.49
PCNB	0.68	0.85	0.49	0.63
Lindane	0.69	0.81	0.44	0.60
Dichloran	0.77	1.29	0.49	0.70
Heptachlor	0.82	0.87	0.78	0.83
Aldrin	1.00	1.00	1.00	1.00
Heptachlor Epoxide	1.54	1.93	1.28	1.43
Endosulfan I	1.95	2.48	1.62	1.79
p,p'-DDE	2.23	2.10	2.00	1.82
Dieldrin	2.40	3.00	1.93	2.12
Captan	2.59	4.09	1.22	1.94
Endrin	2.93	3.56	2.18	2.42
o,p'-DDT	3.16	2.70	2.69	2.39
p,p'-DDD	3.48	3.75	2.61	2.55
Endosulfan II	3.59	4.59	2.25	2.72
p,p'-DDT	4.18	4.07	3.50	3.12
Mirex	6.1	3.78	6.6	4.79
Methoxychlor	7.6	6.5	5.7	4.60
Aldrin (Min. absolute)	3.5	2.6	4.0	5.6

[1]All columns glass, 180 cm x 4 mm ID, solid support Gas-Chrom Q (100/120 mesh)
[2]OV-210 also may be used

8.2 Quantitatively transfer the proper aliquot of sample from the sample container into a two-liter separatory funnel. If less than 800 ml is analyzed, dilute to one liter with interference free distilled water.

9. Extraction

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100 ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K-D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60-ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated (See Section 10).

10. Clean-up and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate

whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to isolate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides. All of the pesticides listed in Scope (1.2) with the exception of mirex are efficiently recovered.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30-ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100-ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100-ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500-ml K-D flask equipped with a 10-ml

ampul. Rinse the separatory funnel and column with three 10-ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether wash- ings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500-ml K-D flasks equipped with 10-ml ampuls (see Eluate Composition 10.4.). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in

petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition - By using an equivalent quantity of any batch of Florisil, as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate

Aldrin	DDT	Mirex
BHC	Heptachlor	PCNB
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin

15% Eluate

Endosulfan I
Endrin
Dieldrin
Dichloran

50% Eluate

Endosulfan II
Captan

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Appendix III.

(1) $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

$$A = \frac{\text{ng standard}}{\text{Standard area}}$$

B = Sample aliquot area
V_i = Volume of extract injected (µl)
V_t = Volume of total extract (µl)
V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

REFERENCES:

1. Monsanto Methodology for Aroclors - Analysis of Environmental Materials for Biphenyls, Analytical Chemistry Method 71-35, Monsanto Company, St. Louis, Missouri, 63166, 1970.

2. "Method for Polychlorinated Biphenyls in Water and Wastewater", this manual, p. 43.

3. "Method for Organophosphorus Pesticides in Water and Wastewater", this manual, p. 25.

4. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", Chapter 6, Section 6.4, U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268, 1973.

5. "Pesticide Analytical Manual", U. S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D. C.

METHOD FOR ORGANOPHOSPHORUS PESTICIDES IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various organophosphorus pesticides in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Azinphos methyl	---
Demeton-O	39560
Demeton-S	---
Diazinon	39570
Disulfoton	39010
Malathion	39530
Parathion methyl	39600
Parathion ethyl	39540

2. Summary

2.1 The method offers several analytical alternatives, dependent on the analyst's assessment of the nature and extent of interferences and the complexity of the pesticide mixtures found. Specifically, the procedure describes the use of an effective co-solvent for efficient sample extraction; provides, through use of the column chromatography and liquid-liquid partition, methods for the elimination of non-pesticide interferences and the preseparation of pesticide mixtures. Identification is made by selective gas chromatographic separation and may be corroborated through the use of two or more unlike columns. Detection and measurement are best accomplished by flame photometric gas chromatography using a

phosphorus specific filter. The electron capture detector, though non-specific, may also be used for those compounds to which it responds. Results are reported in micrograms per liter.

2.2 Confirmation of the identity of the compounds should be made by GC-MS when a new or undefined sample type is being analyzed and the concentration is adequate for such determination.

2.3 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines, causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of organophosphorus pesticides. Sample clean-up procedures are generally required and may result in the loss of certain organophosphorus pesticides. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Compounds such as organochlorine pesticides, polychlorinated biphenyls and phthalate esters interfere with the analysis of organophosphorus pesticides by electron capture gas chromatography. When encountered, these interferences are overcome by the use of the phosphorus specific flame photometric detector. If such a detector is not available, these interferences may be removed from the sample by using the clean-up procedures described in the EPA methods for those compounds (1, 2).

3.4 Elemental sulfur will interfere with the determination of organophosphorus pesticides by flame photometric and electron capture gas chromatography. The elimination of elemental sulfur as an interference is described in Section 10.5, Clean-up and Separation Procedures.

4. Apparatus and Materials

4.1 Gas Crhomatograph - Equipped with glass lined injection port.

4.2 Detector options:

4.2.1 Flame Photometric - 526 mu phosphorus filter.

4.2.2 Electron Capture - Radioactive (tritium or nickel-63).

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long x 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas Chrom Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 OV-1, 3%

4.4.4.2 OV-210, 5%

4.4.4.3 OV-17, 1.5% plus QF-1 or OV-210, 1.95%

4.4.4.4 QF-1 or OV-210, 6% plus SE-30, 4%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three ball (macro) and two ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm x 19 mm ID) with coarse fritted plate and Teflon stopcock on bottom; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 μl.

4.9 Separatory funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.10 Micro-pipets - disposable (140 mm long x 5 mm ID).

4.11 Blender - High speed, glass or stainless steel cup.

4.12 Graduated cylinders - 100 and 250 ml.

4.13 Florisil - PR Grade (60-100 mesh); purchase activated at 1250^{o}F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130^{o}C in foil-covered glass container. Determine lauric-acid value (See Appendix II).

4.14 Alumina - Woelm, neutral; deactivate by pipeting 1 ml of distilled water into 125 ml ground glass-stoppered Erlenmeyer flask. Rotate flask to distribute water over surface of glass. Immediately add 19.0 g fresh alumina through small powder funnel. Shake flask containing mixture for two hours on a mechanical shaker (3).

5. Reagents, Solvents, and Standards

5.1 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.2 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400°C for 4 hrs.).

5.4 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

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., Emslford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.6 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - nanograde, redistill in glass if necessary.

5.7 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\leq$1.5 ng is injected for flame photometric detection and $\leq$ 0.06 ng is injected for electron capture detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several standard pesticides are shown in Figures 1, 2, 3 and 4 and provide reference operating conditions for the four recommended columns.

6.3 The elution order and retention ratios of various organophosphorus pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (4) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 The sample size taken for analysis is dependent on the type of sample and the sensitivity required for the purpose at hand.

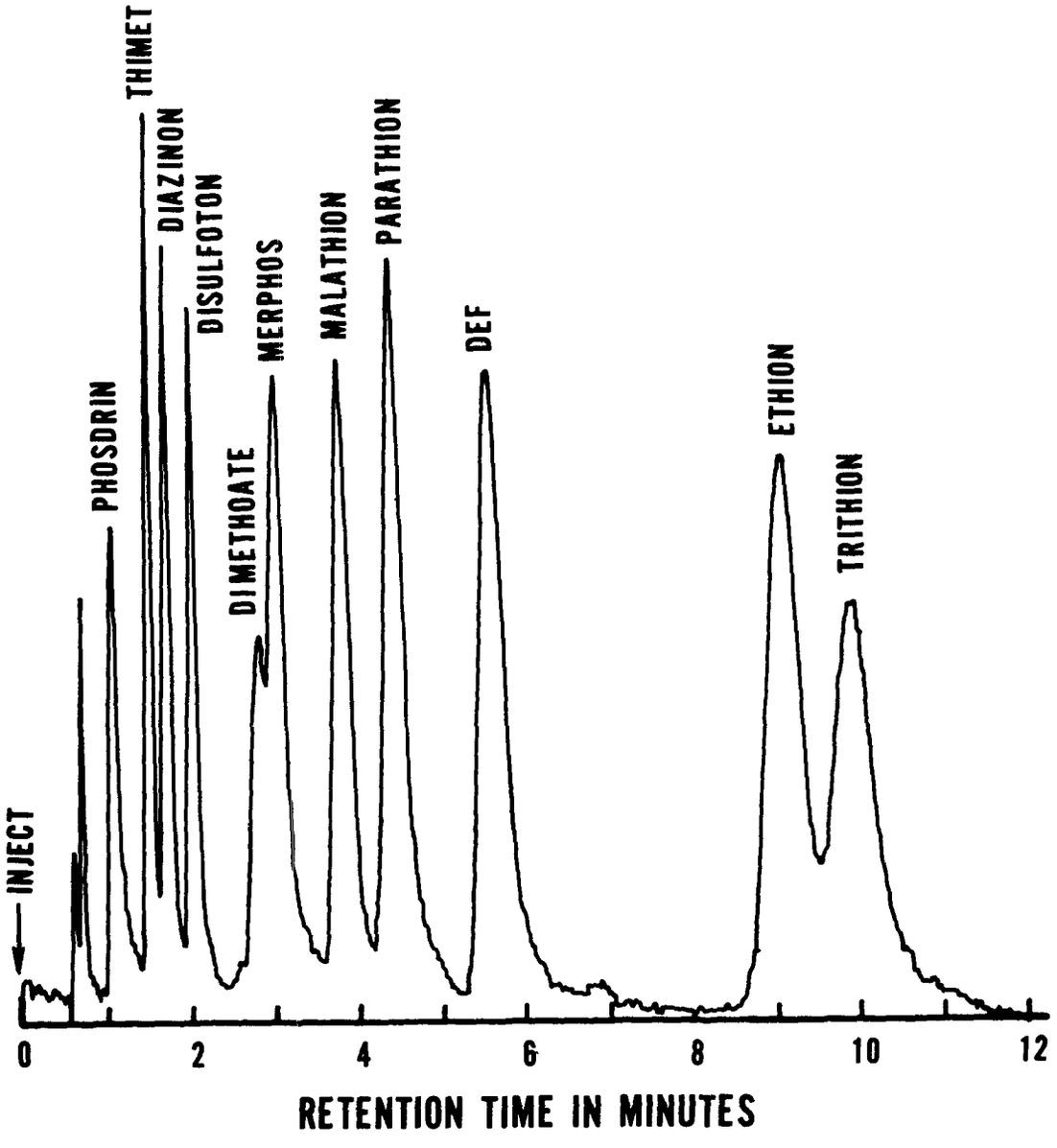

Figure 1. Column Packing: 1.5% OV-17 + 1.95 % QF-1, Carrier Gas: Nitrogen at 70 ml/min, Column Temperature: 215 C, Detector: Flame Photometric (Phosphorus).

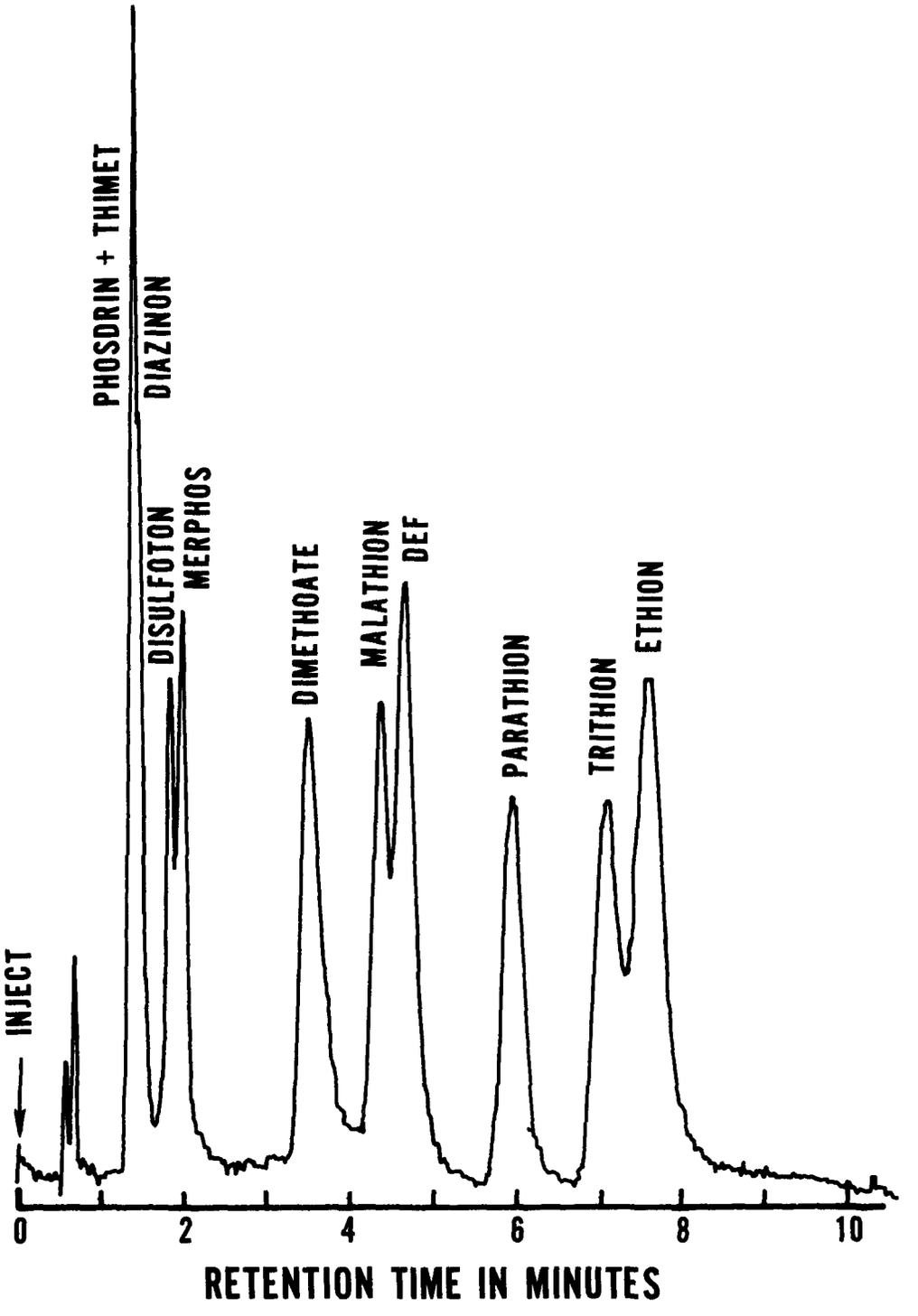

Figure 2. Column Packing: 5% OV-210, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Flame Photometric (Phosphorus).

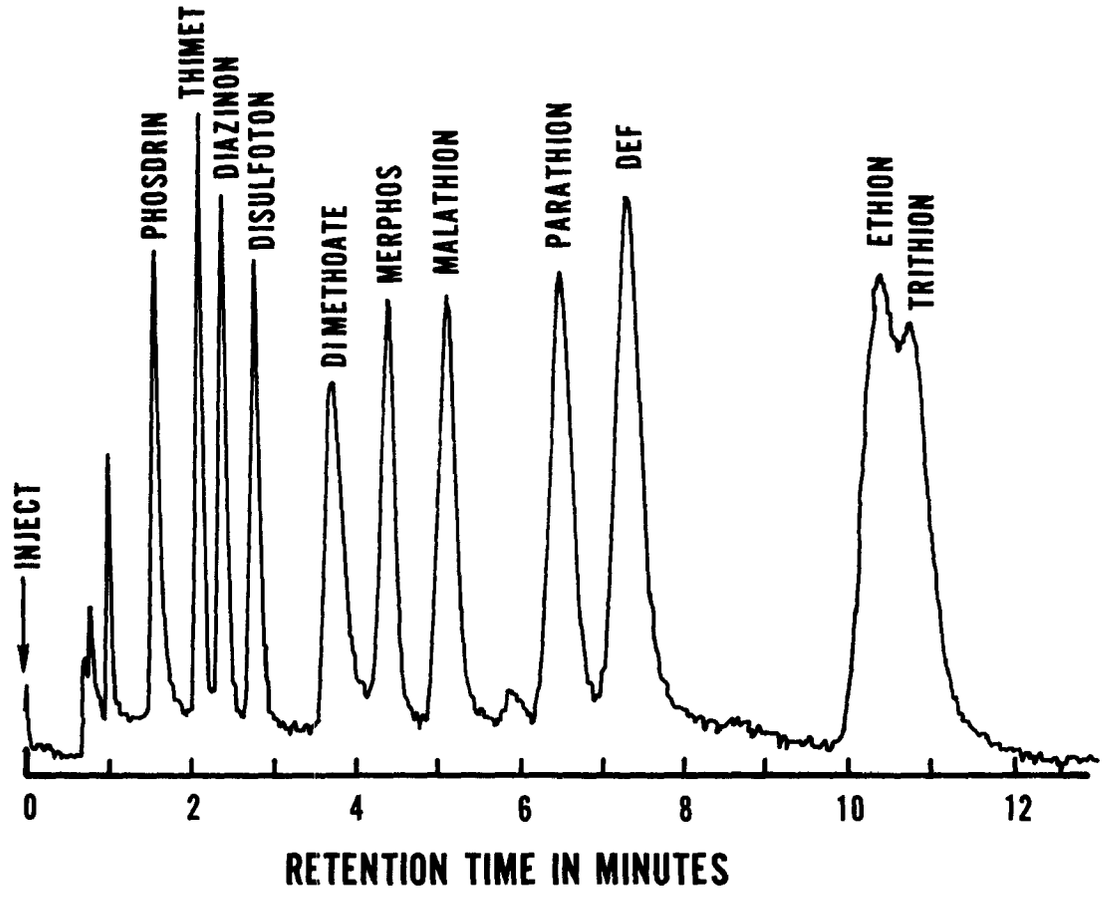

Figure 3. Column Packing: 6% QF-1 + 4% SE-30, Carrier Gas: Nitrogen at 70 ml/min, Column Temperature: 215 C, Detector: Flame Photometric (Phosphorus).

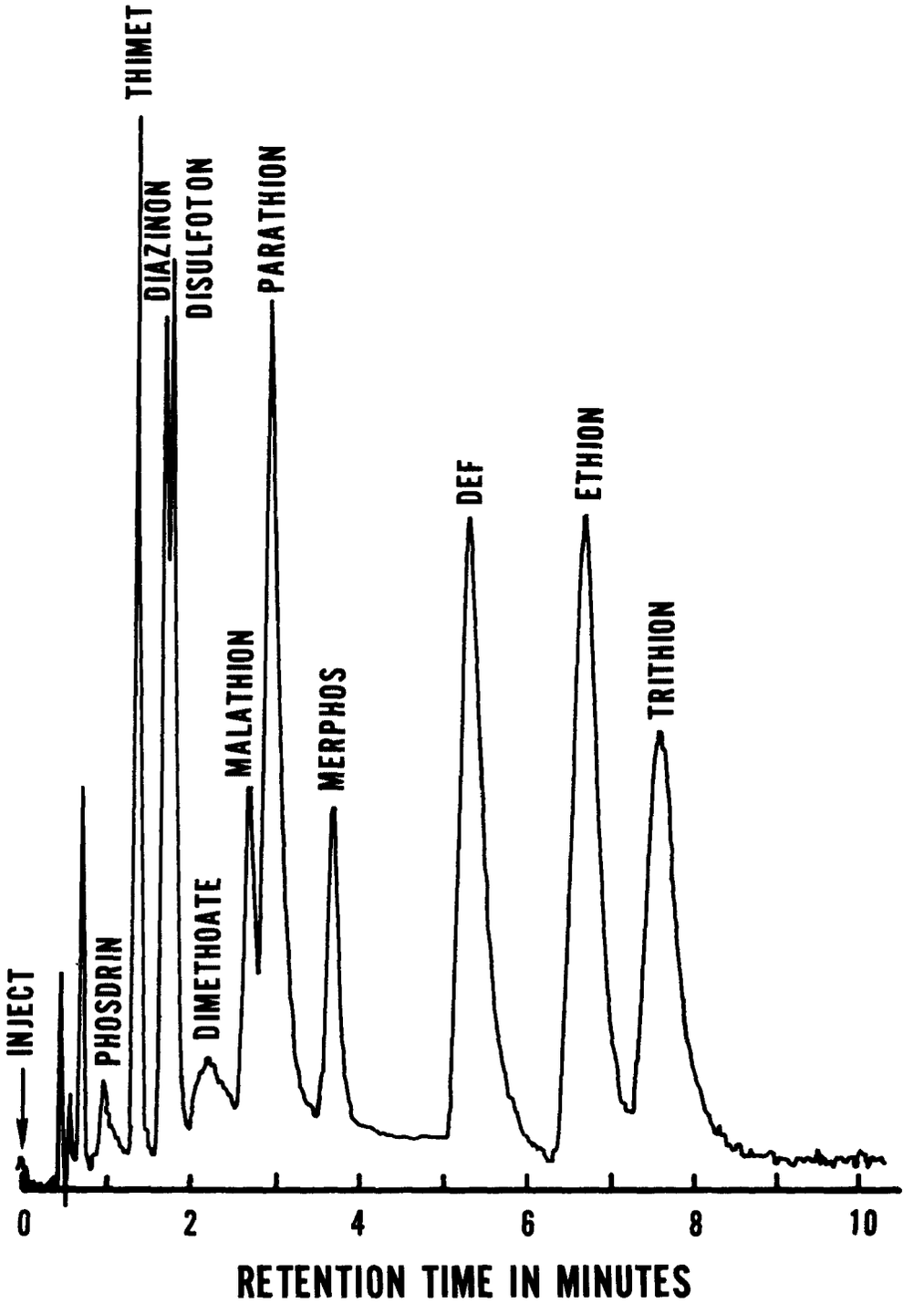

Figure 4. Column Packing: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Flame Photometric (Phosphorus).

TABLE 1

RETENTION TIMES OF SOME ORGANOPHOSPHOROUS PESTICIDES
RELATIVE TO PARATHION

Liquid Phase[1]	1.5% OV-17 + 1.95% QF-1[2]	6% QF-1[2] + 4% SE-30	5% OV-210	7% OV-1
Column Temp.	215 C	215 C	200 C	200 C
Nitrogen Carrier Flow	70 ml/min	70 ml/min	60 ml/min	60 ml/min
Pesticide	RR	RR	RR	RR
Demeton[3]	0.46	0.26 0.43	0.20 0.38	0.74
Diazinon	0.40	0.38	0.25	0.59
Disulfoton	0.46	0.45	0.31	0.62
Malathion	0.86	0.78	0.73	0.92
Parathion methyl	0.82	0.80	0.81	0.79
Parathion ethyl	1.00	1.00	1.00	1.00
Azinphos methyl	6.65	4.15	4.44	4.68
Parathion (min absolute)	4.5	6.6	5.7	3.1

[1]All columns glass, 180 xm x 4 mm ID, solid support Gas-Chrom Q, 100/120 mesh.
[2]May substitute OV-210 for QF-1.
[3]Anomalous, multipeak response often encountered.

Background information on the pesticide levels previously detected at a given sampling site will assist in determining the sample size required, as well as the final volume to which the extract needs to be concen- trated. A 1-liter sample is usually taken for drinking water and ambient water analysis to provide a detection limit of 0.050 to 0.100 µg/l. One-hundred milliliters is usually adequate to provide a detection limit of 1 µg/l for industrial effluents.

8.2 Quantitatively transfer the proper aliquot of sample from the sample container into a two-liter separatory funnel. If less than a 800 ml is analyzed, dilute to one liter with interference free distilled water.

9. Extraction

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100 ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K-D flask equipped with a 10 ml ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60 ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Analyze by gas chromatography unless a need for cleanup is indicated. (See Section 10).

10. Clean-up and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample source will indicate whether clean-up is required. When these interfere with measurement of the pesticides, or affect column life or detector sensitivity, proceed as directed below. The use of these procedures is not required for samples free of interferences. They are provided as options to the analyst to be used when needed.

10.2 Acetonitrile Partition - This procedure is used to separate fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for specific pesticides.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30 ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two

100 ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100 ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500-ml K-D flask equipped with a 10-ml ampul. Rinse the separatory funnel and column with three 10 ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further clean-up is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petro leum 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 petro- leum ether washings. Adjust the elution rate to about 5 ml per minute and,

separately, collect up to four eluates in 500-ml K-D flasks equipped with 10-ml ampuls. (See Eluate Composition, 10.4.) Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric-acid value, the pesticides will be separated into the eluates indicated below:

6% Eluate	15% Eluate
Demeton	Diazinon
Disulfoton	Malathion (trace)
	Parathion Methyl
50% Eluate	**100% Eluate**
Malathion	Azinphos methyl (80%)
Azinphos methyl (20%)	

For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

10.5 Removal of Sulfur - If elemental sulfur interferes with the gas chromatographic analysis, it can be removed by the use of an alumina microcolumn.

10.5.1 Adjust the sample extract volume to 0.5 ml in a K-D

apparatus, using a two-ball Snyder microcolumn.

10.5.2 Plug a disposable pipet with a small quantity of glass wool. Add enough alumina to produce a 3-cm column after settling. Top the alumina with a 0.5-cm layer of anhydrous sodium sulfate.

10.5.3 Quantitatively transfer the concentrated extract to the alumina microcolumn using a 100 µl syringe. Rinse the ampul with 200 µl of hexane and add to the microcolumn.

10.5.4 Elute the microcolumn with 3 ml of hexane and discard the first eluate which contains the elemental sulfur.

10.5.5 Next elute the column with 5 ml of 10% hexane in methylene chloride. Collect the eluate in a 10 ml graduated ampul.

10.5.6 Analyze by gas chromatography.

NOTE: If the electron capture detector is to be used methylene chloride must be removed. To do this, attach the ampul to a K-D apparatus (500-ml flask and 3-ball Snyder column) and concentrate to about 0.5 ml. Adjust volume as required prior to analysis.

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Appendix III.

(1) Micrograms/liter = $\frac{(A)\quad(B)\quad(V_t)}{(V_i)\quad(V_s)}$

A = $\frac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

REFERENCES:

1. "Method for Chlorinated Hydrocarbons in Water and Wastewater", this manual, p. 7.

2. "Method for Polychlorinated Biphenyls (PCBs) in Water and Wastewater", this manual, p. 43.

3. Law, L. M. and Georlitz, D. F., "Microcolumn Chromatographic Clean-up for the Analysis of Pesticides in Water", Journal of the Association for Analytical Chemists, 53, 1276 (1970).

4. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", Chapter 6, Section 6.4, U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268, 1973.

5. "Pesticide Analytical Manual", U. S. Dept. of Health, Education and Welfare, Food and Drug Administration, Washington, D. C.

METHOD FOR POLYCHLORINATED BIPHENYLS (PCBs) IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various polychlorinated biphenyl (PCB) mixtures in water and wastewater.

1.2 The following mixtures of chlorinated biphenyls (Aroclors) may be determined by this method:

Parameter	Storet No.
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

1.3 The method is an extension of the Method for Chlorinated Hydrocarbons in Water and Wastewater (1). It is designed so that determination of both the PCBs and the organochlorine pesticides may be made on the same sample.

2. Summary

2.1 The PCBs and the organochlorine pesticides are co-extracted by liquid-liquid extraction and, insofar as possible, the two classes of compounds separated from one another prior to gas chromatographic determination. A combination of the standard Florisil column cleanup procedure and a silica gel microcolumn separation procedure (2)(3) are employed. Identification is

made from gas chromatographic patterns obtained through the use of two or more unlike columns. Detection and measurement is accomplished using an electron capture, microcoulometric, or electrolytic conductivity detector. Techniques for confirming qualitative identification are suggested.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and the purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and pose great difficulty in obtaining accurate and precise measurement of PCBs and organochlorine pesticides. Separation and clean-up procedures are generally required and may result in the loss of certain organochlorine compounds. Therefore, great care should be exercised in the selection and use of methods for eliminating or minimizing interferences. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Phthalate esters, certain organophosphorus pesticides, and elemental sulfur will interfere when using electron capture for detection. These materials do not interfere when the

microcoulometric or electrolytic conductivity detectors are used in the halogen mode.

3.4 Organochlorine pesticides and other halogenated compounds constitute interferences in the determination of PCBs. Most of these are separated by the method described below. However, certain compounds, if present in the sample, will occur with the PCBs. Included are: Sulfur, Heptachlor, aldrin, DDE, technical chlordane, mirex, and to some extent, o,p'-DDT and p,p'-DDT.

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel-63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long X 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas-Chrom Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 SE-30 or OV-1, 3%

4.4.4.2 OV-17, 1.5% + QF-1 or OV-210, 1.95%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three-ball (macro) and two-ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250-ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Column Pyrex - constructed according to Figure 1.

4.9 Capillary pipets disposable (5-3/4 *in.*) with rubber bulb (Scientific Products P5205-1).

4.10 Low pressure regulator - 0 to 5 PSIG - with low-flow needle valve (see Figure 1, Matheson Model 70).

4.11 Beaker - 100 ml

4.12 Micro Syringes - 10, 25, 50 and 100 ul.

4.13 Separatory funnels - 125 ml, 1000 ml and 2000 ml with Teflon stopcock.

4.14 Blender - High speed, glass or stainless steel cup.

4.15 Graduated cylinders - 100 and 250 ml.

4.16 Florisil - PR Grade (60-100 mesh); purchase activated at 1250^{o}F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each

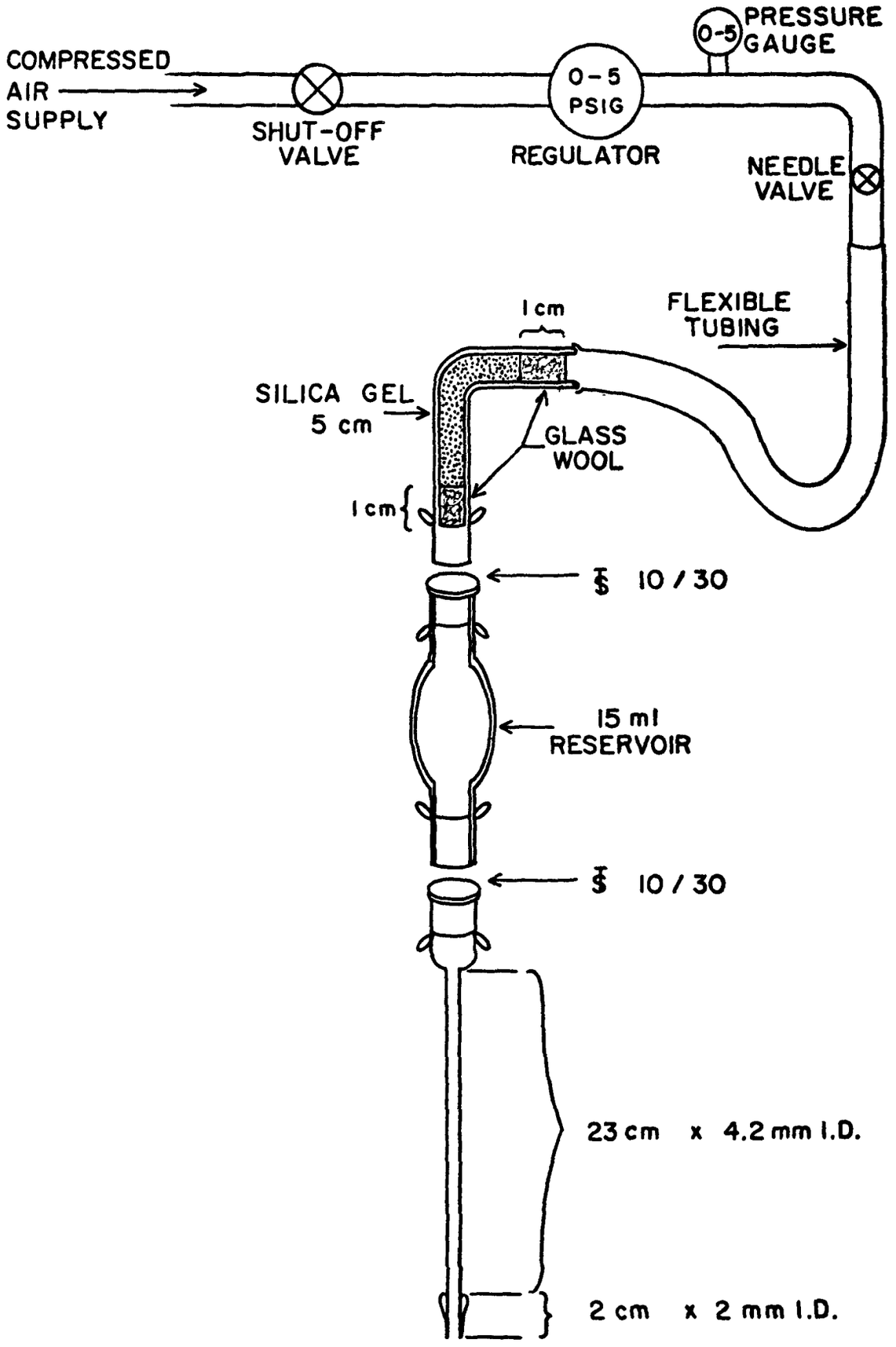

FIGURE 1. MICROCOLUMN SYSTEM

batch overnight at 130°C in foil-covered glass container. Determine lauric-acid value (See Appendix II).

4.17 Silica gel - Davison code 950-08008-226 (60/200 mesh).

4.18 Glass Wool - Hexane extracted.

4.19 Centrifuge Tubes - Pyrex calibrated (15 ml).

5. Reagents, Solvents, and Standards

5.1 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.2 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400° C for 4 hrs.).

5.4 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.5 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523).

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.6 n-Hexane - Pesticide quality (NOT MIXED HEXANES).

5.7 Acetonitrile, Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - pesticide quality, redistill in glass if necessary.

5.8 Standards - Aroclors 1221, 1232, 1242, 1248, 1254, 1260, and 1016.

5.9 Anti-static Solution - STATNUL, Daystrom, Inc., Weston Instrument Division, Newark, N.J., 95212.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when $\geq$ 0.06 ng is injected for electron capture detection and $\leq$ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards are injected frequently as a check on the stability of operating conditions, detector and column. Example chromatograms are shown in Figures 3 through 8 and provide reference operating conditions.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (4) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH

to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 For sensitivity requirement of 1 µg/l, when using microcoulometric or electrolytic conductivity methods for detection take 1000 ml of sample for analysis. If interferences pose no problem, the sensitivity of the electron capture detector should permit as little as 100 ml of sample to be used. Background information on the extent and nature of interferences will assist the analyst in choosing the required sample size and preferred detector.

8.3 Quantitatively transfer the proper aliquot into a two-liter separatory funnel and dilute to one liter.

9. Extraction

9.1 Add 60 ml of 15% methylene chloride in hexane (v:v) to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the mixed solvent to separate from the sample, then draw the water into a one-liter Erlenmeyer flask. Pour the organic layer into a 100-ml beaker and then pass it through a column containing 3-4 inches of anhydrous sodium sulfate, and collect it in a 500-ml K-D flask equipped with a 10 ml-ampul. Return the water phase to the separatory funnel. Rinse the Erlenmeyer flask with a second 60-ml volume of solvent; add the solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract in the K-D evaporator on a hot water bath.

9.4 Qualitatively analyze the sample by gas chromatography with an electron capture detector. From the response obtained decide:

a. If there are any organochlorine pesticides present.

b. If there are any PCBs present.

c. If there is a combination of a and b.

d. If elemental sulfur is present.

e. If the response is too complex to determine a, b or c.

f. If no response, concentrate to 1.0 ml or less, as required, and repeat the analysis looking for a, b, c, d, and e. Samples containing Aroclors with a low percentage of chlorine, e.g., 1221 and 1232, may require this concentration in order to achieve the detection limit of 1 µg/l. Trace quantities of PCBs are often masked by background which usually occur in samples.

9.5 If condition a exists, quantitatively determine the organochlorine pesticides according to (1).

9.6 If condition b exists, PCBs only are present; no further separation or cleanup is necessary. Quantitatively determine the PCBs according to step 11.

9.7 If condition c exists, compare peaks obtained from the sample to those of standard Aroclors and make a judgment as to which Aroclors may be present. To separate the PCBs from the organochlorine pesticides, continue as outlined in 10.4.

9.8 If condition d exists, separate the sulfur from the sample using the method outlined in 10.3 followed by the method in 10.5.

9.9 If condition e exists, the following macro cleanup and separation procedures (10.2 and 10.3) should be employed and, if necessary, followed by the micro separation procedures (10.4 and 10.5).

10. Cleanup and Separation Procedures

10.1 Interferences in the form of distinct peaks and/or high background in the initial gas chromatographic analysis, as well as the physical characteristics of the extract (color, cloudiness, viscosity) and background knowledge of the sample will indicate whether clean-up is required. When these interfere with measurement of the PCBs, or affect column life or detector sensitivity, proceed as directed below.

10.2 Acetonitrile Partition - This procedure is used to remove fats and oils from the sample extracts. It should be noted that not all pesticides are quantitatively recovered by this procedure. The analyst must be aware of this and demonstrate the efficiency of the partitioning for the compounds of interest.

10.2.1 Quantitatively transfer the previously concentrated extract to a 125-ml separatory funnel with enough hexane to bring the final volume to 15 ml. Extract the sample four times by shaking vigorously for one minute with 30-ml portions of hexane-saturated acetonitrile.

10.2.2 Combine and transfer the acetonitrile phases to a one-liter separatory funnel and add 650 ml of distilled water and 40 ml of saturated sodium chloride solution. Mix thoroughly for 30-45 seconds. Extract with two 100-ml portions of hexane by vigorously shaking about 15 seconds.

10.2.3 Combine the hexane extracts in a one-liter separatory funnel and wash with two 100-ml portions of distilled water. Discard the water layer and pour the hexane layer through a 3-4 inch anhydrous sodium sulfate column into a 500-ml K-D flask equipped with a 10-ml ampul. Rinse the separatory funnel and column with three 10-ml portions of hexane.

10.2.4 Concentrate the extracts to 6-10 ml in the K-D evaporator in a hot water bath.

10.2.5 Analyze by gas chromatography unless a need for further cleanup is indicated.

10.3 Florisil Column Adsorption Chromatography

10.3.1 Adjust the sample extract volume to 10 ml.

10.3.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to three eluates in 500-ml K-D flasks equipped with 10-ml ampuls (see Eluate Composition 10.4.). Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.3.1 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated as follows.

6% Eluate

Aldrin	DDT	Pentachloro-nitrobenzene
BHC	Heptachlor	
Chlordane	Heptachlor Epoxide	Strobane
DDD	Lindane	Toxaphene
DDE	Methoxychlor	Trifluralin
	Mirex	PCBs

15% Eluate	50% Eluate
Endosulfan I	Endosulfan II
Endrin	Captan
Dieldrin	
Dichloran	
Phthalate esters	

Certain thiophosphate pesticides will occur in each of the above fractions as well as the 100% fraction. For additional information regarding eluate composition, refer to the FDA Pesticide Analytical Manual (5).

10.3.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath.

10.3.5 Analyze by gas chromatography.

10.4 Silica Gel Micro-Column Separation Procedure (6)

10.4.1 Activation for Silica Gel

10.4.1.1 Place about 20 gm of silica gel in a 100-ml beaker. Activate at 180°C for approximately 16 hours. Transfer the silica gel to a 100-ml glass-stoppered bottle. When cool, cover with about 35 ml of 0.50% diethyl ether in benzene (volume:volume). Keep bottle well sealed. If silica gel collects on the ground glass surfaces, wash off with the above solvent before resealing. Always maintain an excess of the mixed solvent in bottle (aproximately 1/2 in. above silica gel). Silica gel can be effectively stored in this manner for several days.

10.4.2 Preparation of the Chromatographic Column

10.4.2.1 Pack the lower 2 mm ID section of the micro-column with glass wool. Permanently mark

the column 120 mm above the glass wool. Using a clean rubber bulb from a disposable pipet seal the lower end of the microcolumn. Fill the microcolumn with 0.50% ether in benzene (v:v) to the bottom of the 10/30 joint (Figure 1). Using a disposable capillary pipet, transfer several aliquots of the silica gel slurry into the microcolumn. After approximately 1 cm of silica gel collects in the bottom of the microcolumn, remove the rubber bulb seal, tap the column to insure that the silica gel reaches the 120 ± 2 mm mark. Be sure that there are no air bubbles in the column. Add about 10 mm of sodium sulfate to the top of the silica gel. Under low humidity conditions, the silica gel may coat the sides of the column and not settle properly. This can be minimized by wiping the outside of the column with an anti-static solution.

10.4.2.2 Deactivation of the Silica Gel

a. Fill the microcolumn to the base of the 10/30 joint with the 0.50% ether-benzene mixture, assemble reservoir (using spring clamps) and fill with approximately 15 ml of the 0.50% ether-benzene mixture. Attach the air pressure device (using spring

clamps) and adjust the elution rate to approximately 1 ml/min. with the air pressure control. Release the air pressure and detach reservoir just as the last of the solvent enters the sodium sulfate. Fill the column with n-hexane (not mixed hexanes) to the base of the 10/30 fitting. Evaporate all residual benzene from the reservoir, assemble the reservoir section and fill with 5 ml of n-hexane. Apply air pressure and remove the reservoir just as the n-hexane enters the sodium sulfate. The column is now ready for use.

b. Pipet a 1.0 ml aliquot of the concentrated sample extract (previously reduced to a total volume of 2.0 ml) on to the column. As the last of the sample passes into the sodium sulfate layer, rinse down the internal wall of the column twice with 0.25 ml of n-hexane. Then assemble the upper section of the column. As the last of the n-hexane rinse reaches the surface of the sodium sulfate, add enough n-hexane (volume predetermined, see 10.4.3) to just elute all of the PCBs present in the sample. Apply air pressure and adjust until the

flow is 1 ml/min. Collect the desired volume of eluate (predetermined, see 10.4.3) in an accurately calibrated ampul. As the last of the n-hexane reaches the surface of the sodium sulfate, release the air pressure and change the collection ampul.

c. Fill the column with 0.50% diethyl ether in benzene, again apply air pressure and adjust flow to 1 ml/min. Collect the eluate until all of the organochlorine pesticides of interest have been eluted (volume predetermined, see 10.4.3).

d. Analyze the eluates by gas chromatography.

10.4.3 Determination of Elution Volumes

10.4.3.1 The elution volumes for the PCBs and the pesticides depend upon a number of factors which are difficult to control. These include variation in:

a. Mesh size of the silica gel

b. Adsorption properties of the silica gel

c. Polar contaminants present in the eluting solvent

d. Polar materials present in the sample and sample solvent

e. The dimensions of the microcolumns

Therefore, the optimum elution volume must be experimentally determined each time a factor is changed. To determine the elution volumes, add standard mixtures of Aroclors and pesticides to the column and serially collect 1-ml elution volumes. Analyze the individual eluates by gas chromatography and determine the cut-off volume for n-hexane and for ether-benzene. Figure 2 shows the retention order of the various PCB components and of the pesticides. Using this information, prepare the mixtures required for calibraton of the microcolumn.

10.4.3.2 In determining the volume of hexane required to elute the PCBs the sample volume (1 ml) and the volume of n-hexane used to rinse the column wall must be considered. Thus, if it is determined that a 10.0-ml elution volume is required to elute the PCBs, the volume of hexane to be added in addition to the sample volume but including the rinse volume should be 9.5 ml.

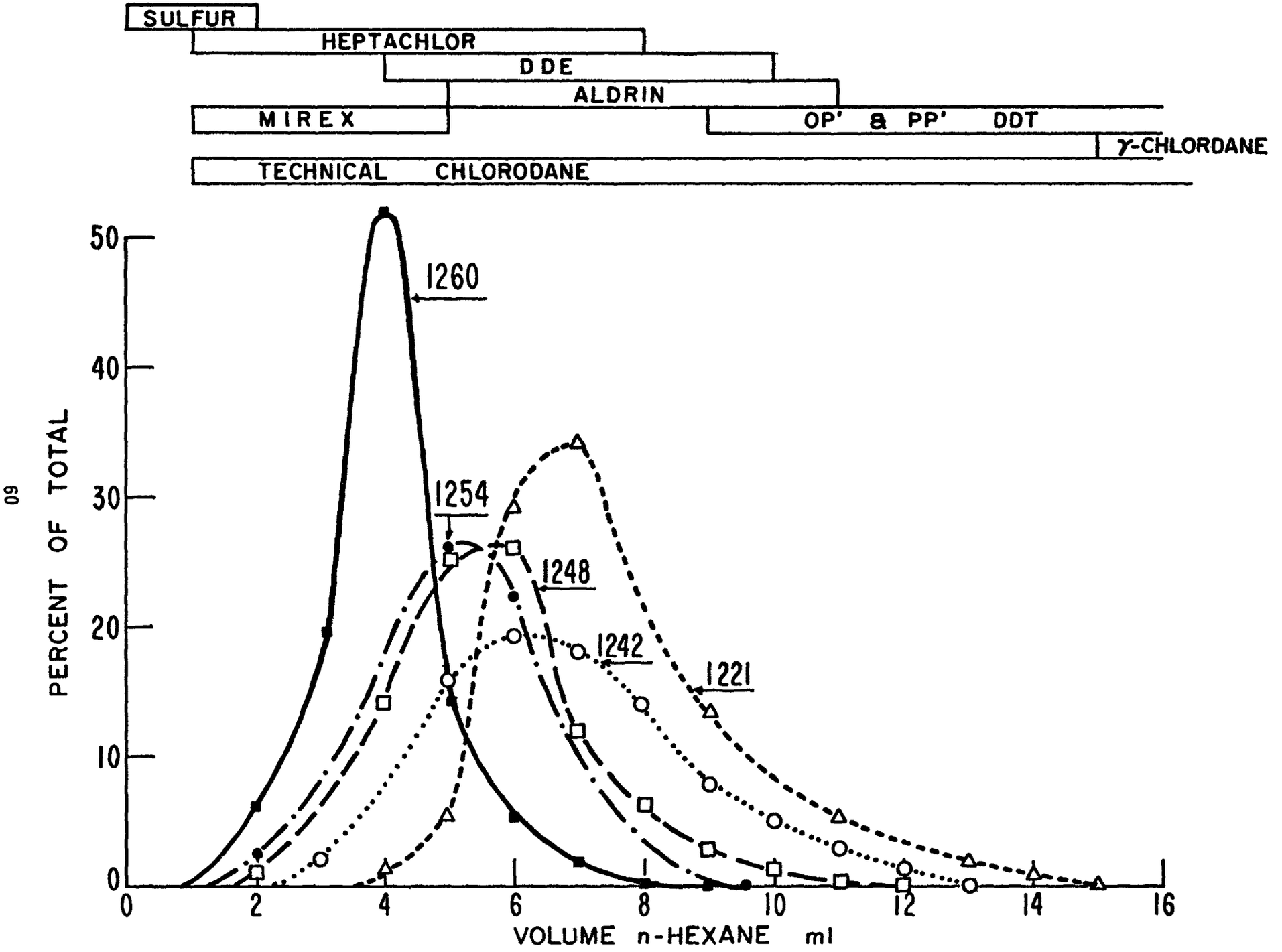

Figure 2. Aroclor Elution Patterns

10.4.3.3 Figure 2 shows that as the average chlorine content of a PCB mixture decreases the solvent volume for complete elution increases. Qualitative determination (9.4) indicates which Aroclors are present and provides the basis for selection of the ideal elution volume. This helps to minimize the quantity of organochlorine pesticides which will elute along with the low percent chlorine PCBs and insures the most efficient separations possible for accurate analysis.

10.4.3.4 For critical analysis where the PCBs and pesticides are not separated completely, the column should be accurately calibrated according to (10.4.3.1) to determine the percent of material of interest that elutes in each fraction. Then flush the column with an additional 15 ml of 0.50% ether in benzene followed by 5 ml of n-hexane and use this reconditioned column for the sample separation. Using this technique one can accurately predict the amount (%) of materials in each micro column fraction.

10.5 Micro Column Separation of Sulfur, PCBs, and Pesticides

10.5.1 See procedure for preparation and packing micro column in PCB analysis section (10.4.1 and 10.4.2).

10.5.2 Microcolumn Calibration

10.5.2.1 Calibrate the microcolumn for sulfur and PCB separation by collecting 1.0-ml fractions and analyzing them by gas chromatography to determine the following:

1) The fraction with the first eluting PCBs (those present in 1260),
2) The fraction with the last eluting PCBs (those present in 1221),
3) The elution volume for sulfur,
4) The elution volume for the pesticides of interest in the 0.50% ether-benzene fraction.

From these data determine the following:

1) The eluting volume containing only sulfur (Fraction I),
2) The eluting volume containing the last of the sulfur and the early eluting PCBs (Fraction II),
3) The eluting volume containing the remaining PCBs (Fraction III),
4) The ether-benzene eluting volume containing the pesticides of interest (Fraction IV).

10.5.3 Separation Procedure

10.5.3.1 Carefully concentrate the 6% eluate from the

florisil column to 2.0 ml in the graduated ampul on a warm water bath.

10.5.3.2 Place 1.0 ml (50%) of the concentrate into the microcolumn with a 1-ml pipet. Be careful not to get any sulfur crystals into the pipet.

10.5.3.3 Collect Fractions I and II in calibrated centrifuge tubes. Collect Fractions III and IV in calibrated ground glass stoppered ampuls.

10.5.3.4 Sulfur Removal (7) - Add 1 to 2 drops of mercury to Fraction II stopper and place on a wrist-action shaker. A black precipitate indicates the presence of sulfur. After approximately 20 minutes the mercury may become entirely reacted or deactivated by the precipitate. The sample should be quantitatively transferred to a clean centrifuge tube and additional mercury added. When crystals are present in the sample, three treatments may be necessary to remove all the sulfur. After all the sulfur has been removedfrom Fraction II (check using gas chromatography) combine Fractions II and III. Adjust the volume to 10 ml and analyze by gas chromatography. Be sure no mercury is transferred to the combined Fractions II and III, since it can react with certain pesticides.

By combining Fractions II and III, if PCBs are present, it is possible to identify the Aroclor(s) present and a quantitative analysis can be performed accordingly. Fraction I can be discarded since it only contains the bulk of the sulfur. Analyze Fractions III and IV for the PCBs and pesticides. If DDT and its homologs, aldrin, heptachlor, or technical chlordane are present along with the PCBs, an additional microcolumn separation can be performed which may help to further separate the PCBs from the pesticides (See 10.4).

11. Quantitative Determination

11.1 Measure the volume of n-hexane eluate containing the PCBs and inject 1 to 5 μl into the gas chromatograph. If necessary, adjust the volume of the eluate to give linear response to the electron capture detector. The microcoulometric or the electrolytic detector may be employed to improve specificity for samples having higher concentrations of PCBs.

11.2 Calculations

11.2.1 When a single Aroclor is present, compare quantitative Aroclor reference standards (e.g., 1242, 1260) to the unknown. Measure and sum the areas of the unknown and the reference Aroclor and calculate the result as follows:

$$\text{Microgram/liter} = \frac{[A]\,[B]\,[V_t]}{[(V_i)\ (Vs)]} \times [N]$$

$$A = \frac{\text{ng of Standard Injected}}{\text{mm}^2} = \frac{ng_2}{mm}$$

B = of Sample Peak Areas - (mm^2)

V_i = Volume of sample injected (µl)

V_t = Volume of Extract (µl) from which sample is injected into gas chromatograph

V_s = Volume of water sample extracted (ml)

N = 2 when micro column used
1 when micro column not used

Peak Area = Peak height (mm x Peak Width at 1/2 height

11.2.2 For complex situatons, use the calibration method described below (8). Small variations in components between different Aroclor batches make it necessary to obtain samples of several specific Aroclors. These reference Aroclors can be obtained from the Southeast Environmental Research Laboratory, EPA, Athens, Georgia, 30601. The procedure is as follows:

11.2.2.1 Using the OV-1 column, chromatograph a known quantity of each Aroclor reference standard. Also chromatograph a sample of p,p'-DDE. Suggested concentration of each standard is 0.1 ng/µl for the Aroclors and 0.02 ng/µl for the p,p'-DDE.

11.2.2.2 Determine the relative retention time (RRT) of each PCB peak in the resulting chromatograms using p,p'-DDE as 100.

$$RRT = \frac{RT \times 100}{RT_{DDE}}$$

RRT = Relative Retention Time

RT = Retention time of peak of interest

RT_{DDE} = Retention time of p,p'-DDE

Retention time is measured as that distance in mm between the first appearance of the solvent peak and the maximum for the compound.

11.2.2.3 To calibrate the instrument for each PCB measure the area of each peak.

Area = Peak height (mm) x Peak width at 1/2 height. Using Tables 1 through 6 obtain the proper mean weight factor, then determine the response factor ng/mm^2.

$$ng/mm^2 = \frac{(ng_i) \quad \frac{(\text{mean weight percent})}{100}}{(\text{Area})}$$

ng_i = ng of Aroclor Standard Injected

Mean weight percent - obtained from Tables 1 through 6.

11.2.2.4 Calculate the RRT value and the area for each PCB peak in the sample chromatogram. Compare the sample chromatogram to those obtained for each reference Aroclor standard. If it is

Table 1

Composition of Aroclor 1221 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
11	31.8	15.8	1	
14	19.3	9.1	1	
16	10.1	9.7	2	
19	2.8	9.7	2	
21	20.8	9.3	2	
28	5.4	13.9	2	85%
			3	15%
32	1.4	30.1	2	10%
			3	90%
37	1.7	48.8	3	
40				

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of seventeen results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 2

Composition of Aroclor 1232 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
11	16.2	3.4	1	
14	9.9	2.5	1	
16	7.1	6.8	2	
20	17.8	2.4	2	
21				
28	9.6	3.4	2	40%
			3	60%
32	3.9	4.7	3	
37	6.8	2.5	3	
40	6.4	2.7	3	
47	4.2	4.1	4	
54	3.4	3.4	3	33%
			4	67%
58	2.6	3.7	4	
70	4.6	3.1	4	90%
			5	10%
78	1.7	7.5	4	
Total	94.2			

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of four results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 3

Composition of Aroclor 1242 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
11	1.1	35.7	1	
16	2.9	4.2	2	
21	11.3	3.0	2	
28	11.0	5.0	2	25%
			3	75%
32	6.1	4.7	3	
37	11.5	5.7	3	
40	11.1	6.2	3	
47	8.8	4.3	4	
54	6.8	2.9	3	33%
			4	67%
58	5.6	3.3	4	
70	10.3	2.8	4	90%
			5	10%
78	3.6	4.2	4	
84	2.7	9.7	5	
98	1.5	9.4	5	
104	2.3	16.4	5	
125	1.6	20.4	5	85%
			6	15%
146	1.0	19.9	5	75%
			6	25%

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 4

Composition of Aroclor 1248 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
21	1.2	23.9	2	
28	5.2	3.3	3	
32	3.2	3.8	3	
47	8.3	3.6	3	
40	8.3	3.9	3	85%
			4	15%
47	15.6	1.1	4	
54	9.7	6.0	3	10%
			4	90%
58	9.3	5.8	4	
70	19.0	1.4	4	80%
			5	20%
78	6.6	2.7	4	
84	4.9	2.6	5	
98	3.2	3.2	5	
104	3.3	3.6	4	10%
			5	90%
112	1.2	6.6	5	
125	2.6	5.9	5	90%
			6	10%
146	1.5	10.0	5	85%
			6	15%
Total	103.1			

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

Table 5

Composition of Aroclor 1254 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
47	6.2	3.7	4	
54	2.9	2.6	4	
58	1.4	2.8	4	
70	13.2	2.7	4	25%
			5	75%
84	17.3	1.9	5	
98	7.5	5.3	5	
104	13.6	3.8	5	
125	15.0	2.4	5	70%
(			6	80%
146	10.4	2.7	5	30%
			6	70%
160	1.3	8.4	6	
174	8.4	5.5	6	
203	1.8	18.6	6	
232	1.0	26.1	7	
Total	100.0			

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent.

[b]Standard deviation of six results as a percentage of the mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers are bracketed.

Table 6

Composition of Aroclor 1260 (8)

RRT[a]	Mean Weight Percent	Relative Std. Dev.[b]	Number of Chlorines[c]	
70	2.7	6.3	5	
84	4.7	1.6	5	
98	3.8	3.5	[d]	
104			5	60%
			6	40%
117	3.3	6.7	6	
125	12.3	3.3	5	15%
			6	85%
146	14.1	3.6	6	
160	4.9	2.2	6	50%
			7	50%
174	12.4	2.7	6	
203	9.3	4.0	6	10%
			7	90%
232			[e]	
244	9.8	3.4	6	10%
			7	90%
280	11.0	2.4	7	
332	4.2	5.0	7	
372	4.0	8.6	8	
448	.6	25.3	8	
528	1.5	10.2	8	
Total	98.6			

[a]Retention time relative to p,p'-DDE=100. Measured from first appearance of solvent. Overlapping peaks that are quantitated as one peak are bracketed.

[b]Standard deviation of six results as a mean of the results.

[c]From GC-MS data. Peaks containing mixtures of isomers of different chlorine numbers are bracketed.

[d]Composition determined at the center of peak 104.

[e]Composition determined at the center of peak 232.

apparent that the PCB peaks present are due to only one Aroclor, then calculate the concentration of each PCB using the following formula:

ng PCB = ng/mm^2 x Area

Where Area = Area (mm^2) of sample peak

ng/mm^2 = Response factor for that peak measured.

Then add the nanograms of PCBs present in the injection to get the total number of nanograms of PCBs present. Use the following formula to calculate the concentration of PCBs in the sample:

Micrograms/Liter =

V_s = volume of water extracted (ml)

V_t = volume of extract (µl)

V_i = volume of sample injected (µl)

ng = sum of all the PCBs in nanograms for that Aroclor identified

N = 2 when microcolumn used

N = 1 when microcolumn not used

The value can then be reported as micrograms/liter PCBs or as the Aroclor. For samples containing more than one Aroclor, use Figure 9 chromatogram divisional flow chart to assign a proper response factor to each peak and also identify the "most likely" Aroclors

present. Calculate the ng of each PCB isomer present and sum them according to the divisional flow chart. Using the formula above, calculate the concentration of the various Aroclors present in the sample.

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

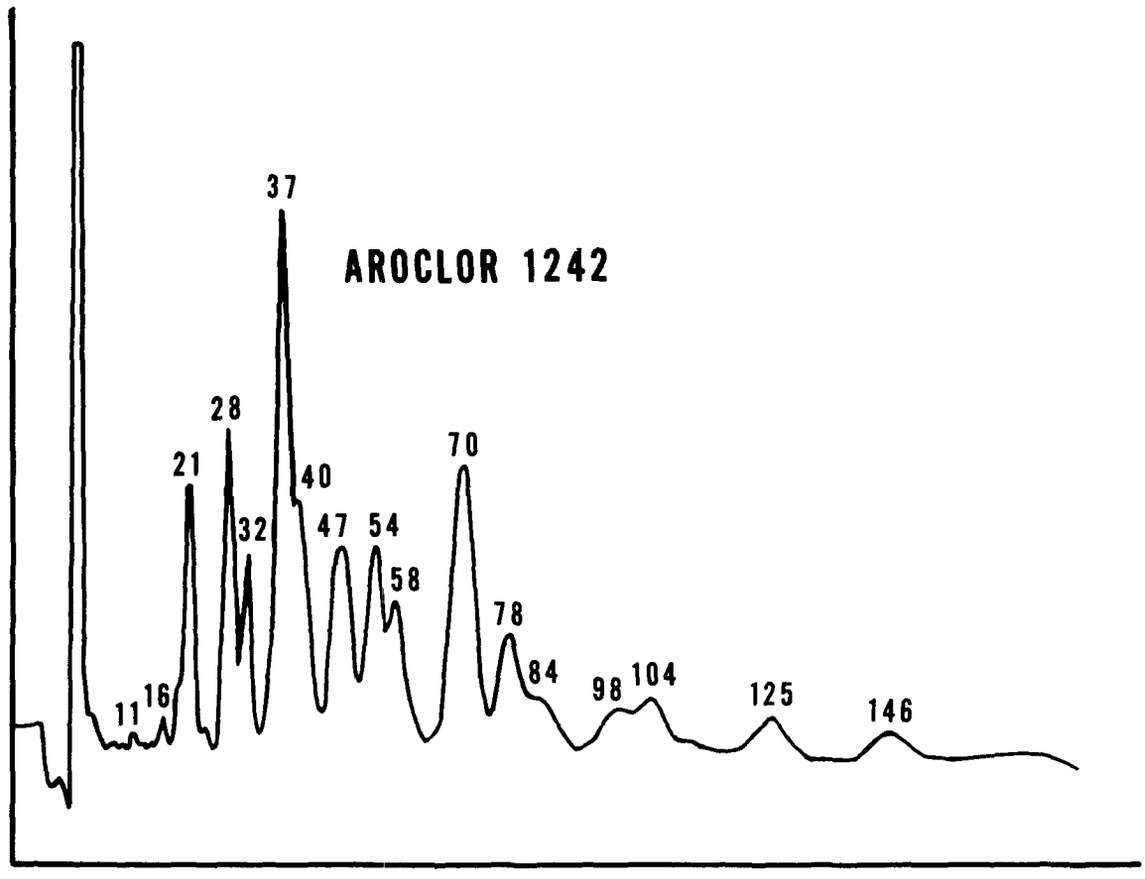

Figure 3. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture

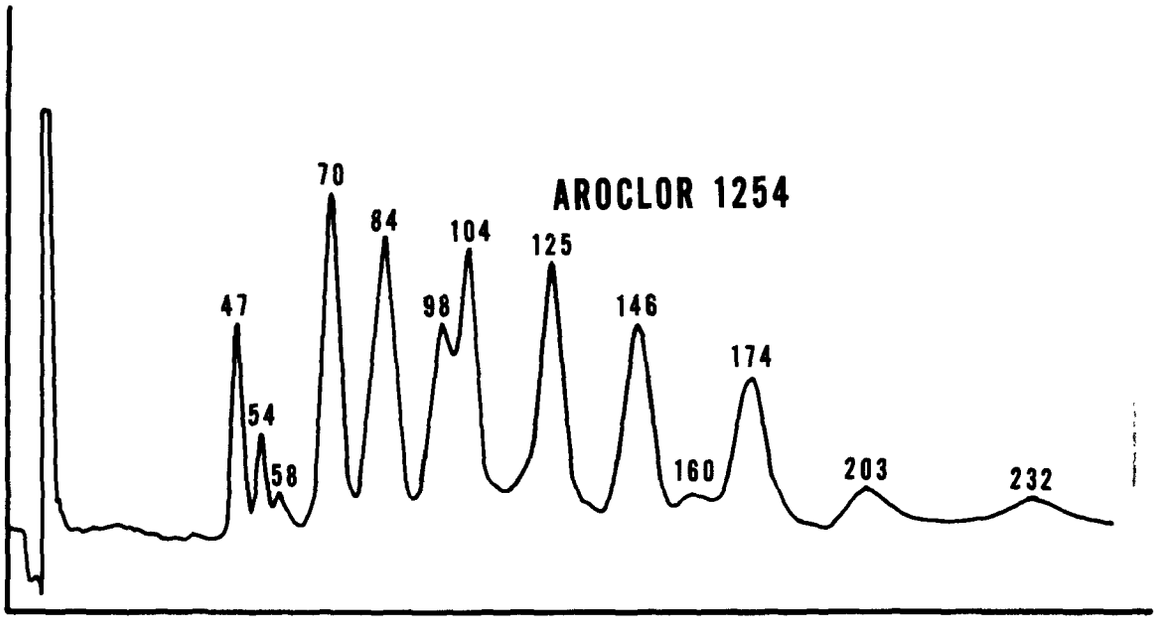

Figure 4. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

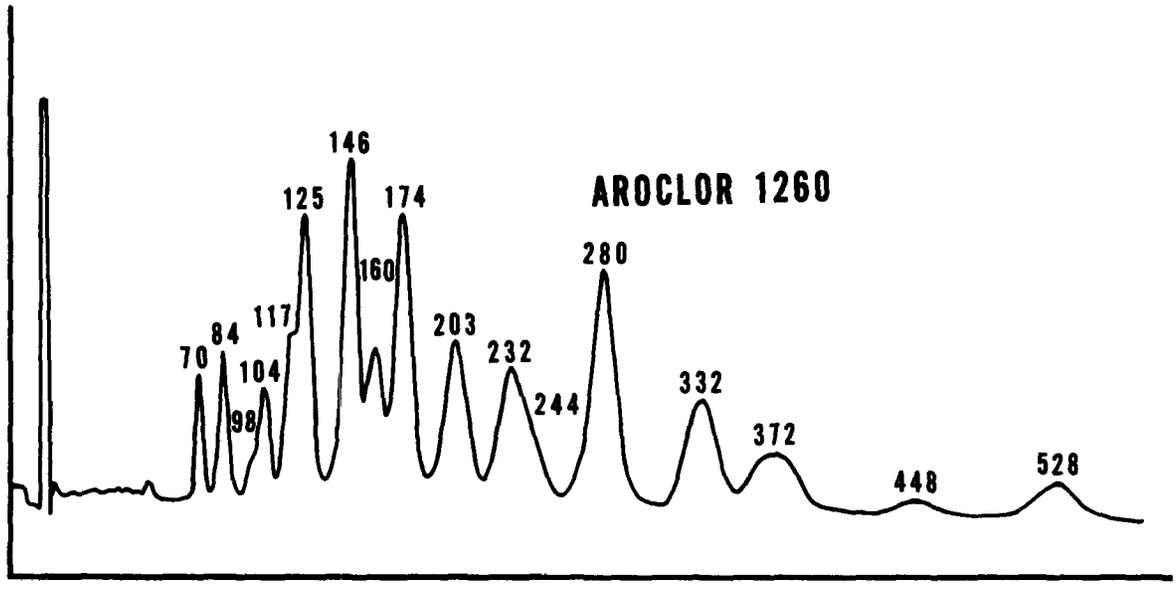

Figure 5. Column: 3% OV-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 170 C, Detector: Electron Capture.

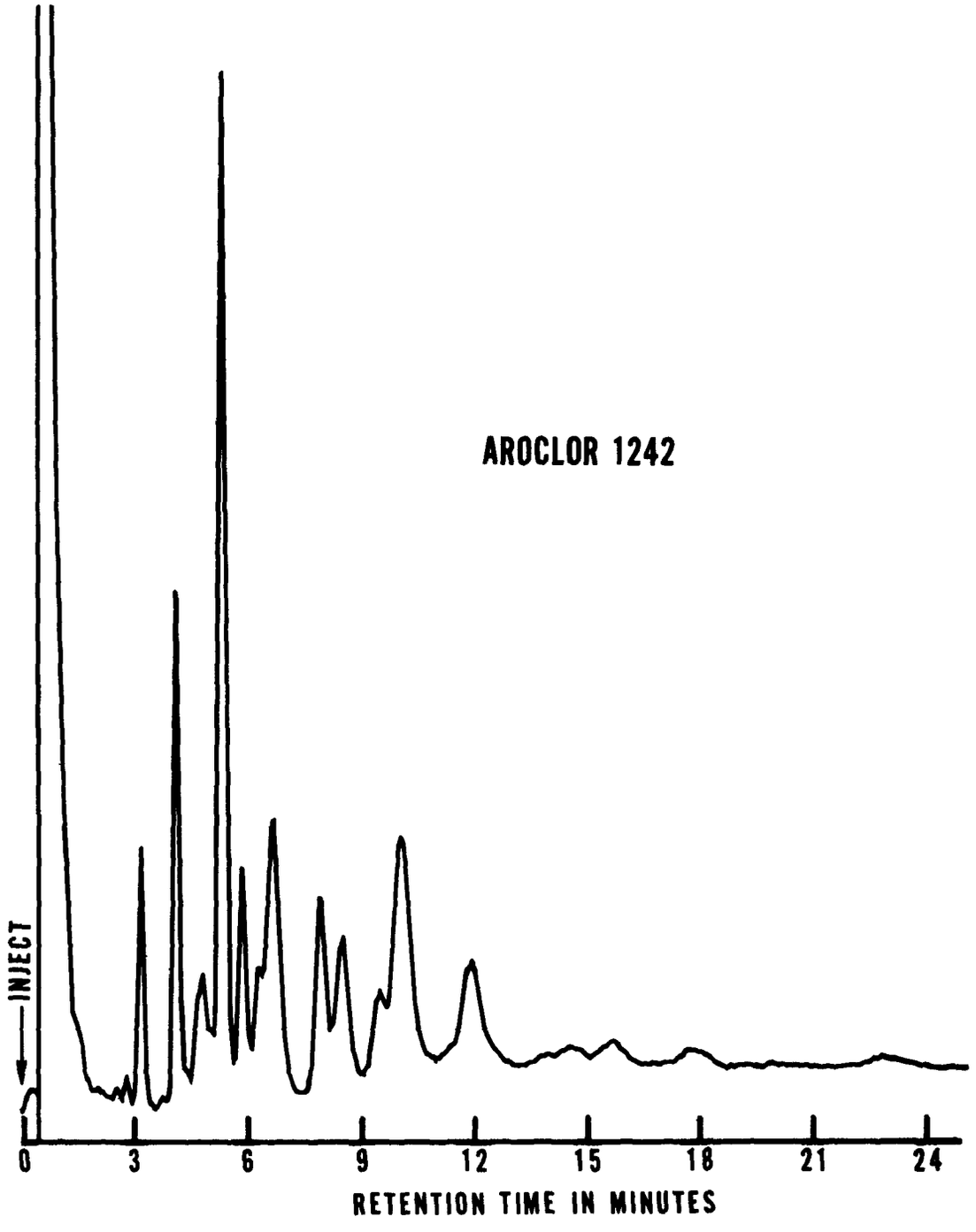

Figure 6. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

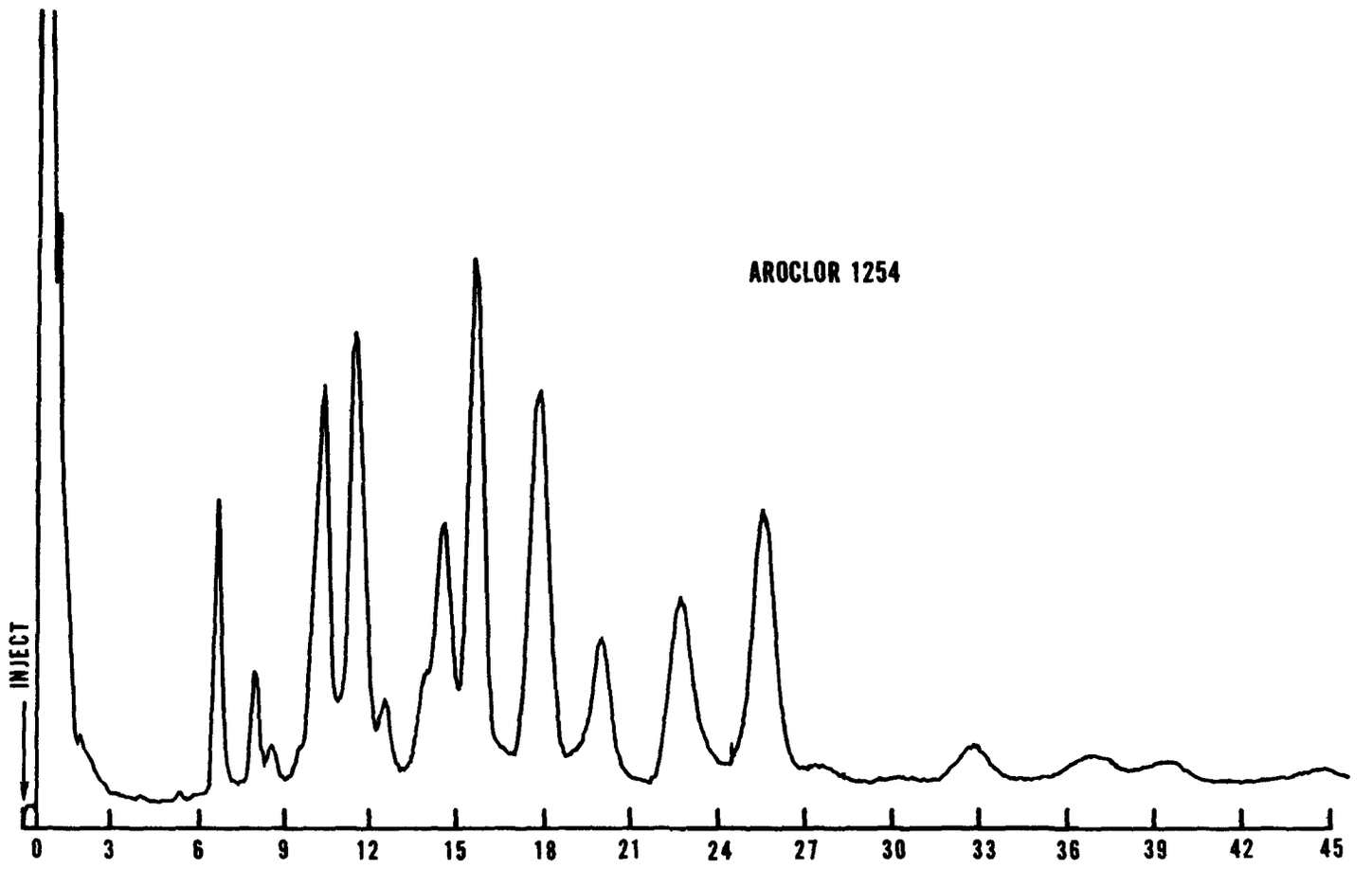

Figure 7. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200 C, Detector: Electron Capture.

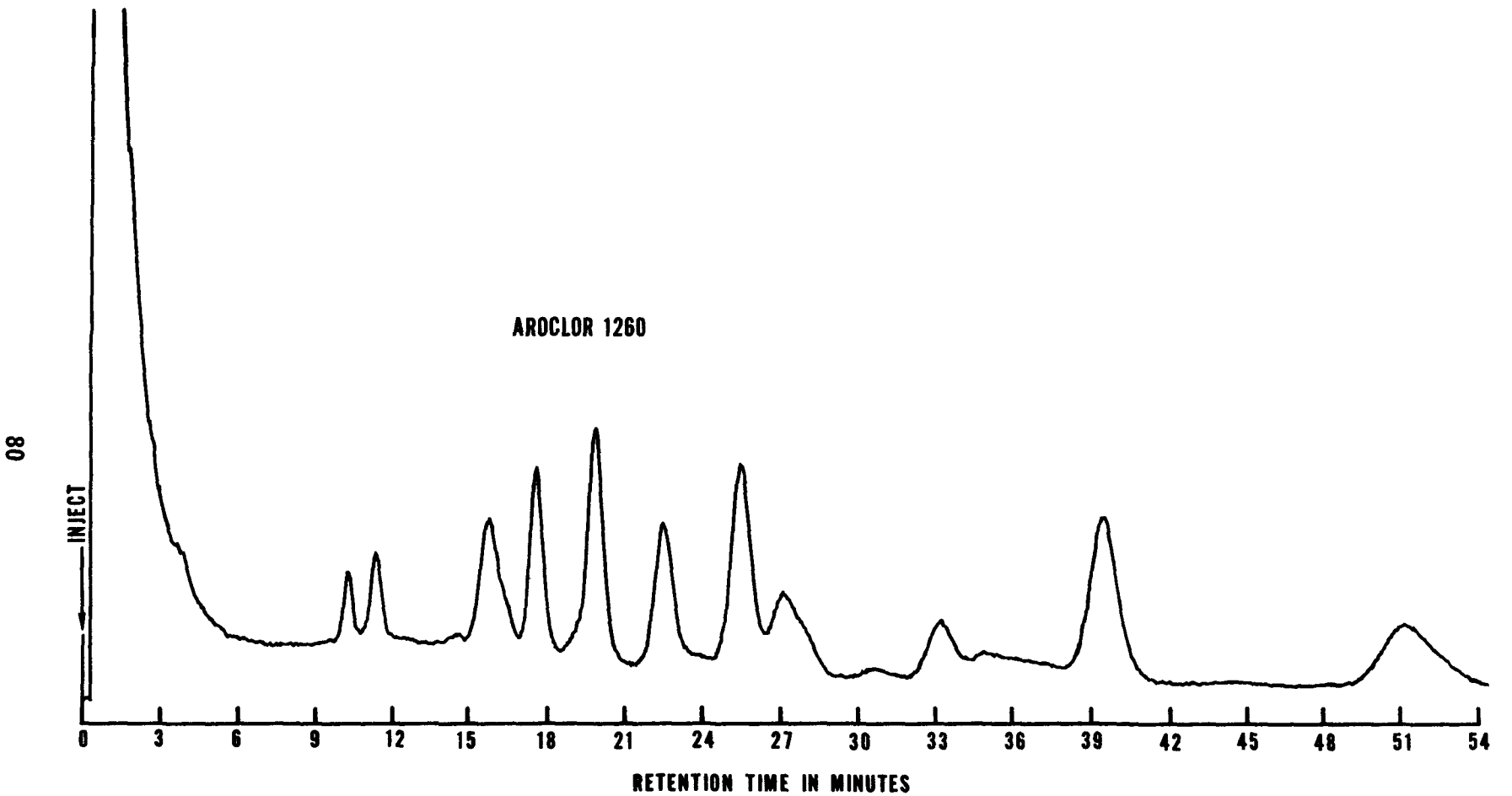

Figure 8. Column: 1.5% OV-17 + 1.95% QF-1, Carrier Gas: Nitrogen at 60 ml/min, Column Temperature: 200C, Detector: Electron Capture.

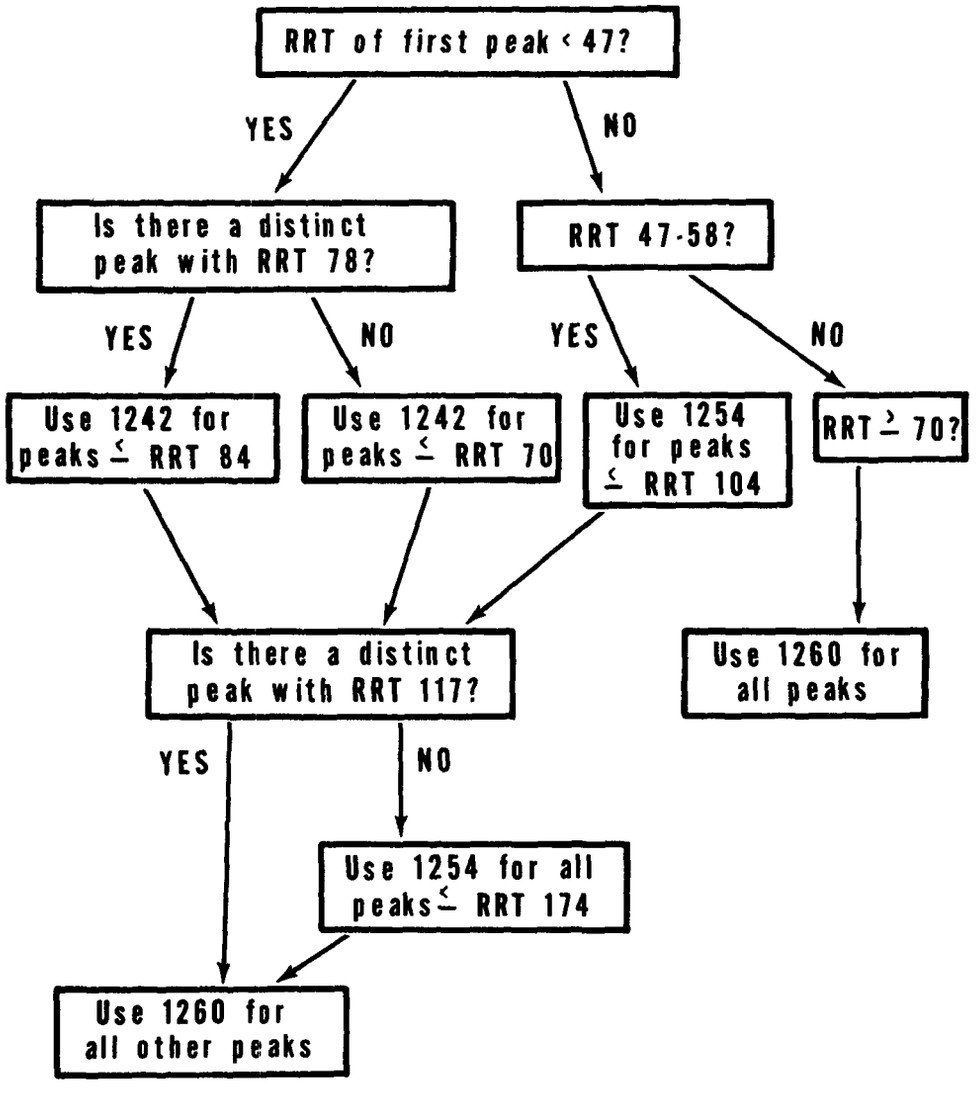

Figure 9. Chromatogram Division Flowchart (8).

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METHOD FOR TRIAZINE PESTICIDES IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various symmetrical triazine pesticides in water and wastewaters.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Ametryn	---
Altraton	---
Atrazine	39033
Prometon	39056
Prometryn	39057
Propazine	39024
Secbumeton	---
Simazine	39055
Terbuthylazine	---

2. Summary

2.1 The method describes an efficient sample extraction procedure and provides, through use of column chromatography, a method for the elimination of non-pesticide interferences and the pre-separation of pesticide mixtures. Identification is made by selective gas chromatographic separation, and measurement is accomplished by the use of an electroytic conductivity detector (CCD) in the nitrogen mode or a nitrogen specific thermionic detector. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of triazine pesticides. The use of a specific detector supported by an optional column cleanup procedure will eliminate many of these interferences.

3.3 Nitrogen containing compounds other than the triazines may interfere.

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options

4.2.1 Electrolytic Conductivity.

4.2.2 Nitrogen specific thermionic

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long x 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas Chrom Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 Carbowax 20M, 1%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three ball (macro) and two ball (micro)

4.5.2 Evaporative Flasks - 500 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm x 19 mm ID) with coarse fritted plate and Teflon stopcock on bottom; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - Pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 μl.

4.9 Separatory funnels - 2000 ml with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Graduated Cylinders - 1000 ml.

4.12 Florisil - PR Grade (60-100 mesh); purchase activated at 1250^{o}F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each

batch overnight at 130°C in foil-covered glass container. Determine lauric acid value (See Appendix II).

5. Reagents, Solvents, and Standards

5.1 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.2 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400 C for 4 hrs.).

5.3 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.4 Diethyl Ether - Pesticide Quality, redistilled in glass, if necessary

5.4.1 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.)

5.4.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.5 Hexane, Methanol, Methylene Chloride, Petroleum Ether (boiling range 30-60°C) - pesticide quality, redistill in glass if necessary.

5.6 Pesticide Standards - Reference grade.

6. Calibration

6.1 Gas chromatographic operating conditions are considered optimum when an injection of $\leq$ 20 ng of each triazine will yield a peak at least 50% of full scale deflection with the modified Coulson detector (1). For all quantitative

measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Inject standards frequently as a check on the stability of operating conditions. A chromatogram of a mixture of several pesticides is shown in Figure 1 and provides reference operating conditions for the recommended column.

6.3 The elution order and retention ratios of various organophosphorus pesticides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (2) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10N sodium hydroxide.

8.2 Quantitatively transfer a 1000 ml aliquot into a two-liter separatory funnel.

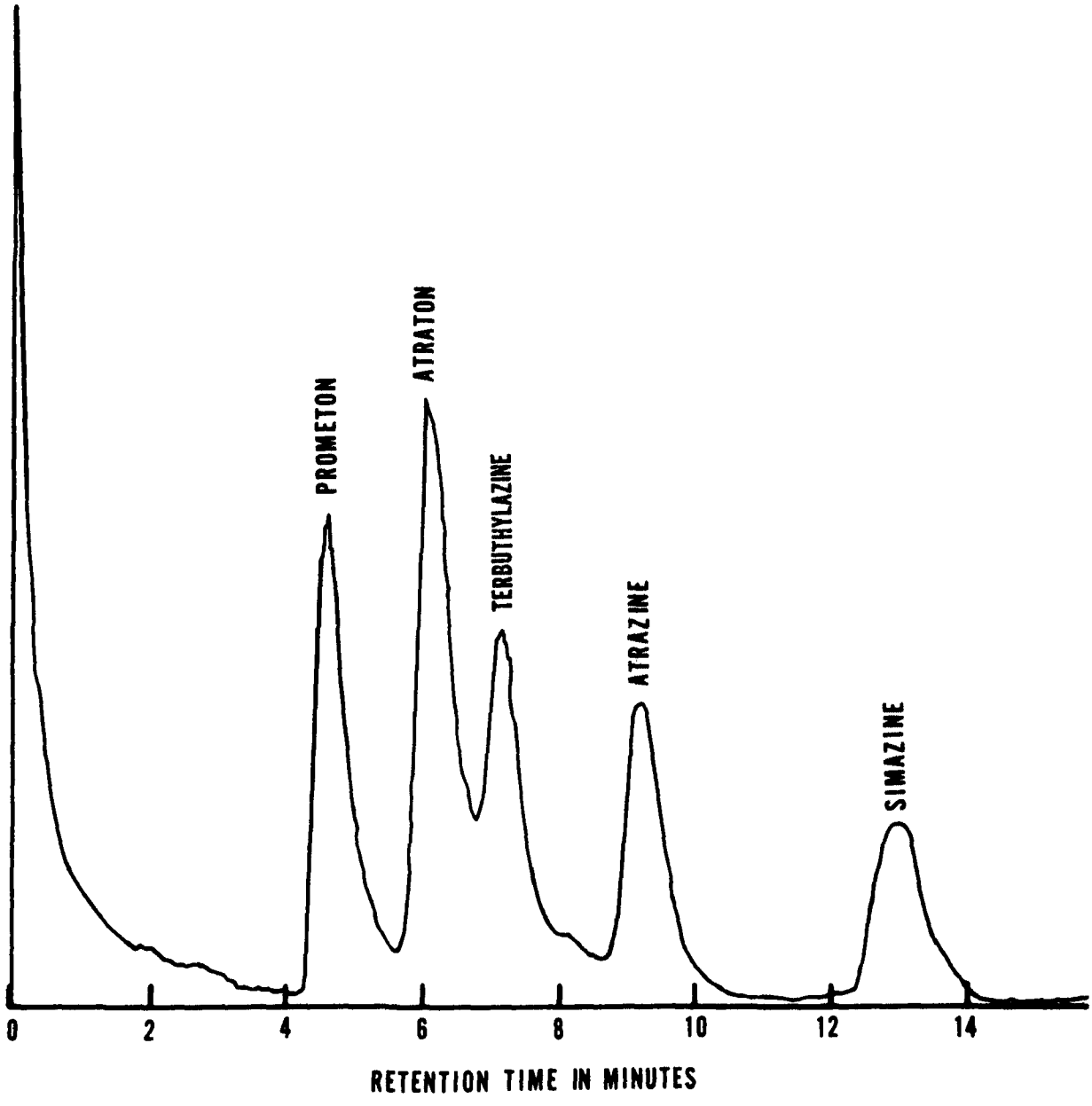

Figure 1. Column Packing: 1% Carbowax 20M on Gas-Chrom Q (100/120 mesh), Column Temperature : 155 C, Carrier Gas: Helium at 80 ml/min, Detector: Electrolytic Conductivity.

TABLE 1

RETENTION RATIOS OF VARIOUS TRIAZINE

PESTICIDES RELATIVE TO ATRAZINE

Pesticide	Retention Ratio
Prometon	0.52
Atraton	0.67
Propazine	0.71
Terbuthylazine	0.78
Secbumeton	0.88
Atrazine	1.00
Prometryne	1.10
Simazine	1.35
Ametryne	1.48

Absolute retention time of atrazine = 10.1 minutes

9. Extraction

9.1 Add 60 ml methylene chloride to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the solvent to separate from the sample, draw the organic layer into a 100-ml beaker, then pass the organic layer through a chromatographic column containing 3-4 inches anhydrous sodium sulfate, and collect it in a 500-ml K-D flask equipped with a 10 ml ampul. Add a second 60-ml volume of solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract to 10 ml in a K-D evaporator on a hot water bath. Disconnect the Snyder column just long enough to add 10 ml hexane to the K-D flask and then continue the concentration to about 5-6 ml. This operation is to displace methylene chloride and give a final hexane solution. If the need for cleanup is indicated, continue to Florisil Column Cleanup (10 below).

9.4 If further cleanup is not required, replace the Snyder column and flask with a micro-Snyder column and continue the concentration to 0.5-1.0 ml. Analyze this final concentrate by gas chromatography.

10. Florisil Column Adsorption Chromatography

10.1 Adjust the sample extract volume to 10 ml.

10.2 Place a charge of activated Florisil (weight determined by lauric acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to four eluates in 500-ml K-D flasks equipped with 10-ml ampuls. (See Eluate Composition, 10.4.) Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.4 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated as follows:

15% Eluate	50% Eluate	100% Eluate
Propazine (90%)	Propazine (10%)	Atraton
Terbuthylazine (30%)	Terbuthylazine(70%)	Secbumeton
Atrazine (20%)	Atrazine (80%)	Prometon
	Ametryne	
	Prometryne	
	Simazine	

10.5 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath. Change to the micro-Snyder column and continue concentration to 0.5-1.0 ml.

10.6 Analyze by gas chromatography.

11. Calculation of Results

11.1 Determine the pesticide concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Appendix III.

(1) $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

$A = \frac{\text{ng standard}}{\text{Standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (µl)

V_t = Volume of total extract (µl)

V_s = Volume of water extracted (ml)

12. Reporting Results

12.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

REFERENCES:

1. Patchett, G. G., "Evaluation of the Electrolytic Conductivity Detector for Residue Analyses of Nitrogen-Containing Pesticides", Journal of Chromatographic Science, 8, 155 (1970).

2. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", Chapter 6, Section 6.4, U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268, 1972. (Revised edition to be available soon.)

METHOD FOR O-ARYL CARBAMATE PESTICIDES IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various O-aryl carbamate pesticides in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Aminocarb	---
Carbaryl	39750
Methiocarb	---
Mexacarbate	---
Propoxur	---

2. Summary

2.1 A measured volume of water is extracted with methylene chloride. The concentrated extract is cleaned up with a Florisil column. Appropriate fractions from the column are concentrated and portions are separated by thin-layer chromatography. The carbamates are hydrolyzed on the layer and the hydrolysis products are reacted with 2,6-dibromoquinone chlorimide to yield specific colored products. Quantitative measurement is achieved by visually comparing the responses of sample extracts to the responses of standards on the same thin-layer. Identifications are confirmed by changing the pH of the layer and observing color changes of the reaction products. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Direct interferences may be encountered from phenols that may be present in the sample. These materials react with the chromogenic reagent and yield reaction products similar to those of the carbamates. In cases where phenols are suspected of interfering with a determination, a different solvent system should be used to attempt to isolate the carbamates.

3.2 Indirect interferences may be encountered from naturally colored materials whose presence masks the chromogenic reaction.

4. Apparatus and Materials

4.1 Thin-layer plates - Glass plates (200 x 200 mm) coated with 0.25 mm layer of Silica Gel G (gypsum binder).

4.2 Spotting Template

4.3 Developing Chamber

4.4 Sprayer - 20 ml capacity

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

4.5.1 Snyder Column - three ball (K-503000)

4.5.2 Micro-Snyder Column - two ball (K-569001)

4.5.3 Evaporative Flasks - 500 ml (K-570001)

4.5.4 Receiver Ampuls - 10 ml graduated (K-570050)

4.5.5 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - Pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 μl.

4.9 Separatory Funnel - 2000 ml, with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Florisil - PR Grade (60-80 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch overnight at 130°C in foil-covered glass container. Determine lauric acid value (see Appendix II).

5. Reagents, Solvents, and Standards

5.1 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.2 Sodium Sulfate - (ACS) Granular, anhydrous.

5.3 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.4 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.4.1 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.)

5.4.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.5 Hexane, Methanol, Methylene Chloride, Petroleum Ether - nanograde, redistill in glass if necessary.

5.6 Pesticide Standards - Reference grade.

5.8.1 TLC Standards - 0.100 µg/ul in chloroform.

5.7 Chromogenic agent - Dissolve 0.2 g 2,6-dibromoquinone chlorimide in 20 ml chloroform.

5.8 Buffer solution - 0.1 N sodium borate in water.

6. Calibration

6.1 To insure even solvent travel up the layer, the tank used for layer development must be thoroughly saturated with developing solvent before it is used. This may be achieved by lining the inner walls of the tank with chromatography paper and introducing the solvent 1-2 hours before use.

6.2 Samples and standards should be introduced to the layer using a syringe, micropipet or other suitable device that permits all the spots to be about the same size and as small as possible. An air stream directed on the layer during spotting will speed solvent evaporation and help to maintain small spots.

6.3 For qualitative and quantitative work, spot a series representing 0.1-1.0 µg of a pesticide. Tables 1 and 2 present color responses and R_f values for several solvent systems.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts should be developed and used as a check on the analytical system. Quality control

Table 1

R_f Values of O-Aryl Carbamate Pesticides in Several Solvent Systems

	A	B	C	D	E	F
Carbaryl	0.26	0.22	0.48	0.41	0.58	0.24
Aminocarb	0.26	0.02	0.46	0.52	0.54	0.04
Mexacarbate	0.34	0.22	0.54	0.53	0.60	0.24
Methiocarb	0.31	0.31	0.55	0.55	0.59	0.28
Propoxur	0.27	0.10	0.53	0.59	0.60	0.13

Solvent Systems:

A. Hexane/acetone (3:1)
B. Methylene chloride
C. Benzene/acetone (4:1)
D. Benzene/cyclohexane/diethylamine (5:2:2)
E. Ethyl acetate
F. Chloroform

Table 2

Color Responses and Detection Limit for O-Aryl Carbamates

	Colors:		Detection Limit (ug)
	Before Buffer	After Buffer	
Carbaryl	Brown	Red-Purple	0.1
Aminocarb	Gray	Green	0.1
Mexacarbate	Gray	Green	0.1
Methiocarb	Brown	Tan	0.2
Propoxur	Blue	Blue	0.1

check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 Quantitatively transfer a one-liter aliquot into a two-liter separatory funnel.

9. Extraction

9.1 Add 60 ml of methylene chloride to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the solvent to separate from the sample, draw the organic layer into a 100-ml beaker, then pass the organic layer through a chromatographic column containing 3-4 inches anhydrous sodium sulfate, and collect it in a 500-ml K-D flask equipped with a 10-ml ampul. Add a second 60-ml volume of solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract to 10 ml in a K-D evaporator on a hot water bath. Disconnect the Snyder column just long enough to add 10 ml of hexane to the K-D flask and then continue the concentration to about 5-6 ml. If the need for cleanup is indicated, continue to Florisil Column Cleanup (10 below).

9.4 If further cleanup is not required, replace the Snyder column and flask with a micro-Snyder column and continue the concentration to 0.5-1.0 ml. Analyze this final concentrate by thin-layer chromatography (Section 11).

10. Florisil Column Cleanup

10.1 Adjust the sample extract to 10 ml with hexane.

10.2 Place a charge of activated Florisil (weight determined by lauric-acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately collect the four eluates in 500-ml K-D flasks equipped with 10-ml ampuls. Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.1 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated as follows:

50% Eluate	100% Eluate
Carbaryl (70%)	Carbaryl (30%)
Mexacarbate	Aminocarb
	Propoxur

10.4 Concentrate the eluates to 6 - 10 ml in the K-D evaporator in a hot water bath. Change to the micro-Snyder column and continue concentration to 0.5-1.0 ml.

10.5 Analyze according to 11. below.

11. Separation and Detection

11.1 Carefully spot 10% of the extract on a thin layer. On the same plate spot several pesticides or mixtures for screening purposes, or a series of 1, 2, 4, 6, 8 and 10 µl of specific standards for quantitative analysis.

11.2 Develop the layers 10 cm in a tank saturated with solvent vapors. Remove the plate and allow it to dry.

11.3 Spray the layer rapidly and evenly with about 10-15 ml chromogenic reagent. Heat the layer in an oven at 110°C for 15 minutes. The pesticides will appear with colors as indicated in Table 2. Make quantitative estimates by visually comparing the intensity and size of the spots with those of the series of standards.

11.4 Spray the layer with sodium borate reagent and observe the color shift of the reaction products. The color shift must be the same for sample and standard for identification to be confirmed.

12. Calculation of Results

12.1 Determine the concentration of pesticide in a sample by comparing the response in a sample to that of a quantity of standard treated on the same layer. Divide the result, in micrograms, by the fraction of extract spotted to convert to micrograms per liter.

13. Reporting Results

13.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

METHOD FOR N-ARYL CARBAMATE AND UREA PESTICIDES IN WATER AND WASTEWATER

1. Scope and Application

1.1 This method covers the determination of various N-aryl carbamate and urea pesticides in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
Barban	---
Chlorpropham	---
Diuron	39650
Fenuron	---
Fenuron-TCA	---
Linuron	---
Monuron	---
Monuron-TCA	---
Neburon	---
Propham	39052
Siduron	---
Swep	---

2. Summary

2.1 A measured volume of water is extracted with methylene chloride and the concentrated extract is cleaned up with a Florisil column. Appropriate fractions from the column are concentrated and portions are separated by thin-layer chromatography. The pesticides are hydrolyzed to primary amines, which in turn are chemically converted to diazonium salts. The layer is sprayed with 1-naphthol and the products appear as colored spots. Quantitative measurement is achieved by visually comparing the

responses of sample extracts to the responses of standards on the same thin layer. Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Direct interferences may be encountered from aromatic amines that may be present in the sample. These materials react with the chromogenic reagent and yield reaction products similar to those of the pesticides. In cases where amines are suspected of interfering with a determination, a different solvent system should be used to attempt to isolate the pesticides on the layer.

3.2 Indirect interferences may be encountered from naturally colored materials whose presence masks the chromogenic reaction.

4. Apparatus and Materials

4.1 Thin-layer plates - Glass plates (200 x 200 mm) coated with 0.25 mm layer of Silica Gel G (gypsum binder).

4.2 Spotting Template

4.3 Developing Chamber

4.4 Sprayer - 20 ml capacity

4.5 Kuderna-Danish (K-D) Glassware (Kontes)

4.5.1 Snyder Column - three ball (K-503000)

4.5.2 Micro-Snyder Column - two ball (K-569001)

4.5.3 Evaporative Flasks - 500 ml (K-570001)

4.5.4 Receiver Ampuls - 10 ml graduated (K-570050)

4.5.5 Ampul Stoppers

4.6 Chromatographic Column - Chromaflex (400 mm long x 19 mm ID) with coarse fritted plate on bottom and Teflon stopcock; 250 ml reservoir bulb at top of column with flared out funnel shape at top of bulb - a special order (Kontes K-420540-9011).

4.7 Chromatographic Column - Pyrex (approximately 400 mm long x 20 mm ID) with coarse fritted plate on bottom.

4.8 Micro Syringes - 10, 25, 50 and 100 µl.

4.9 Separatory Funnel - 2000 ml, with Teflon stopcock.

4.10 Blender - High speed, glass or stainless steel cup.

4.11 Florisil - PR Grade (60-80 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch overnight at 130°C in foil-covered glass container. Determine lauric acid value (see Appendix II).

5. Reagents, Solvents, and Standards

5.1 Sodium Chloride - (ACS) Saturated solution in distilled water (pre-rinse NaCl with hexane).

5.2 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.3 Sodium Sulfate - (ACS) Granular, anhydrous (conditioned at 400°C for 4 hrs.).

5.4 Sulfuric Acid - (ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.5 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.6 Hexane, Methanol, Methylene Chloride, Petroleum Ether - nanograde, redistill in glass if necessary.

5.7 Pesticide Standards - Reference grade.

5.9.1 TLC Standards - 0.100 µg/µl in chloroform.

5.8 Nitrous acid - prepare just before use by mixing 1 g $NaNO_2$ with 20 ml 0.2 N HCl.

5.9 Chromogenic agent - dissolve 1.0 g 1-Naphthol in 20 ml ethanol. Prepare fresh daily.

6. Calibration

6.1 To insure even solvent travel up the layer, the tank used for layer development must be thoroughly saturated with developing solvent before it is used. This may be achieved by lining the inner walls of the tank with chromatography paper and introducing the solvent 1-2 hours before use.

6.2 Samples and standards should be introduced to the layer using a syringe, micropipet or other suitable device that permits all the spots to be about the same size and as small as possible. An air stream directed on the layer during spotting will speed solvent evaporation and help to maintain small spots.

6.3 For qualitative and quantitative work, spot a series representing 0.1-1.0 µg of a pesticide. Tables 1 and 2 present color responses and R_f values for several solvent systems.

TABLE 1

R_f VALUES OF N-ARYL CARBAMATE AND UREA PESTICIDES
IN SEVERAL SOLVENT SYSTEMS

Carbamates	A	B	C	D	E	F	G
Propham	0.49	0.54	0.73	0.48	0.36	0.68	0.69
Chloropropham	0.57	0.60	0.73	0.49	0.37	0.70	0.73
Barban	0.61	0.59	0.72	0.41	0.28	0.70	0.74
Swep	0.48	0.44	0.70	0.41	0.28	0.67	0.66
Urea							
Fenuron	0.03	0.04	0.38	0.22	0.10	0.41	0.30
Fenuron-TCA	0.03	0.04	0.36	0.22	0.10	0.41	0.30
Monuron	0.04	0.05	0.37	0.24	0.10	0.47	0.34
Monuron-TCA	0.04	0.06	0.34	0.24	0.10	0.46	0.34
Diuron	0.05	0.09	0.38	0.28	0.13	0.54	0.44
Linuron	0.40	0.43	0.62	0.39	0.24	0.66	0.64
Neburon	0.21	0.28	0.64	0.41	0.26	0.68	0.65
Siduron	0.02	0.07	0.68	0.39	0.25	0.62	0.55

Solvent Systems:

A. Methylene chloride
B. Chloroform
C. Ethyl Acetate
D. Hexane/acetone (2:1)
E. Hexane/acetone (4:1)
F. Chloroform/acetonitrile (2:1)
G. Chloroform/acetonitrile (5:1)

TABLE 2

COLOR RESPONSES AND DETECTION LIMIT FOR THE N-ARYL CARBAMATES AND UREAS

Carbamates	Color	Detection Limit (ug)
Propham	Red-purple	0.2
Chlorpropham	Purple	0.1
Barban	Purple	0.05
Swep	Blue-purple	0.2
Ureas		
Fenuron	Red-purple	0.05
Fenuron-TCA	Red-purple	0.1
Monuron	Pink-orange	0.05
Monuron-TCA	Pink-orange	0.1
Diuron	Blue-purple	0.1
Linuron	Blue-purple	0.1
Neburon	Blue-purple	0.1
Siduron	Red-purple	0.05

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (1) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 Blend the sample if suspended matter is present and adjust pH to near neutral (pH 6.5-7.5) with 50% sulfuric acid or 10 N sodium hydroxide.

8.2 Quantitatively transfer a one-liter aliquot into a two-liter separatory funnel.

9. Extraction

9.1 Add 60 ml of methylene chloride to the sample in the separatory funnel and shake vigorously for two minutes.

9.2 Allow the solvent to separate from the sample, draw the organic layer into a 100-ml beaker, then pass the organic layer through a chromatographic column containing 3-4 inches anhydrous sodium sulfate, and collect it in a 500-ml K-D flask equipped with a 10-ml ampul. Add a second 60-ml volume of solvent to the separatory funnel and complete the extraction procedure a second time. Perform a third extraction in the same manner.

9.3 Concentrate the extract to 10 ml in a K-D evaporator on a hot water bath. Disconnect the Snyder column just long enough to add 10-ml hexane to the K-D flask and then continue the concentration to about 5-6 ml. If the need for cleanup is indicated, continue to Florisil Column Cleanup (10 below).

9.4 If further cleanup is not required, replace the Snyder column and flask with a micro-Snyder column and continue the concentration to 0.5-1.0 ml. Analyze this final concentrate by thin-layer chromatography (Section 11).

10. Florisil Column Cleanup

10.1 Adjust the sample extract to 10 ml with hexane.

10.2 Place a charge of activated Florisil (weight determined by lauric acid value, see Appendix II) in a Chromaflex column. After settling the Florisil by tapping the column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.3 Pre-elute the column, after cooling, with 50-60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Adjust the elution rate to about 5 ml per minute and, separately, collect up to four eluates in 500-ml K-D flasks equipped with 10-ml ampuls. (See Eluate Composition, 10.3.1.) Perform the first elution with 200 ml of 6% ethyl ether in petroleum ether, and the second elution with 200 ml of 15% ethyl ether in petroleum ether. Perform the third elution with 200 ml

of 50% ethyl ether - petroleum ether and the fourth elution with 200 ml of 100% ethyl ether.

10.3.1 Eluate Composition - By using an equivalent quantity of any batch of Florisil as determined by its lauric acid value, the pesticides will be separated into the eluates indicated below:

15% Eluate	50% Eluate	100% Eluate
Chlorpropham	Barban (5%)	Neburon (92%)
Propham	Linuron	Diuron
Barban (95%)	Neburon (8%)	Monuron
		Siduron

CAUTION: Fenuron and Fenuron-TCA are not recovered from the Florisil column.

10.4 Concentrate the eluates to 6-10 ml in the K-D evaporator in a hot water bath. Change to the micro-Snyder column and continue concentration to 0.5-1.0 ml.

10.5 Analyze according to 11. below.

11. Separation and Detection

11.1 Carefully spot 10% of the extract on a thin layer. On the same plate spot several pesticides or mixtures for screening purposes, or a series of 1, 2, 4, 6, 8 and 10 μl of specific standards for quantitative analysis.

11.2 Develop the layers 10 cm in a tank saturated with solvent vapors. Remove the plate and allow it to dry.

11.3 Spray the layer rapidly and evenly with about 10-15 ml sulfuric acid solution. Heat the layer in an oven at 110^{o}C for 15 minutes.

11.4 When the layer is cool, spray it with nitrous acid reagent and allow it to dry. Spray the layer with 1-naphthol reagent and allow it to dry again. The pesticides will appear as purple spots (see Table 2). Identifications are made by comparison of colors and R_f values. Quantitative estimates are made by visually comparing the intensity and size of the spots with those of the series of standard.

12. Calculation of Results

12.1 Determine the concentration of pesticide in a sample by comparing the response in a sample to that of a quantity of standard treated on the same layer. Divide the result, in micrograms, by the fraction of extract spotted to convert to micrograms per liter.

13. Reporting Results

13.1 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

REFERENCES:

1. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories", Chapter 6, Section 6.4, U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268, 1972.

METHOD FOR CHLOROPHENOXY ACID PESTICIDES IN WATER AND WASTEWATERS

1. Scope and Application

1.1 This method covers the determination of various chlorinated phenoxy acid pesticides in water and wastewater.

1.2 The following pesticides may be determined individually by this method:

Parameter	Storet No.
2,4-D	---
Dicamba	---
Silvex	39760
2,4,5-T	---

1.3 Since these compounds may occur in water in various forms (i.e., acid, salt, ester, etc.) a hydrolysis step is included to permit the determination of the active part of the herbicide.

2. Summary

2.1 Chlorinated phenoxy acids and their esters are extracted from the acidified water sample with ethyl ether. The esters are hydrolyzed to acids and extraneous organic material is removed by a solvent wash. The acids are converted to methyl esters which are extracted from the aqueous phase. The extract is cleaned by passing it through a micro-adsorption column. Identification of the esters is made by selective gas chromatographic separations and may be corroborated through the use of two or more unlike columns. Detection and measurement is accomplished by electron capture, microcoulometric or

electrolytic conductivity gas chromatography (1). Results are reported in micrograms per liter.

2.2 This method is recommended for use only by experienced pesticide analysts or under the close supervision of such qualified persons.

3. Interferences

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Appendix I.

3.2 The interferences in industrial effluents are high and varied and often pose great difficulty in obtaining accurate and precise measurement of chlorinated phenoxy acid herbicides. Sample clean-up procedures are generally required and may result in loss of certain of these herbicides. It is not possible to describe procedures for overcoming all of the interferences that may be encountered in industrial effluents.

3.3 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols including chlorophenols will also interfere with this procedure.

3.4 Alkaline hydrolysis and subsequent extraction eliminates many of the predominant chlorinated insecticides which might otherwise interfere with the test.

3.5 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Glassware and glass wool should be acid-rinsed and sodium sulfate should be acidified with sulfuric acid to avoid this possibility.

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with glass lined injection port.

4.2 Detector Options:

4.2.1 Electron Capture - Radioactive (tritium or nickel-63)

4.2.2 Microcoulometric Titration

4.2.3 Electrolytic Conductivity

4.3 Recorder - Potentiometric strip chart (10 in.) compatible with the detector.

4.4 Gas Chromatographic Column Materials:

4.4.1 Tubing - Pyrex (180 cm long X 4 mm ID)

4.4.2 Glass Wool - Silanized

4.4.3 Solid Support - Gas-Chrom-Q (100-120 mesh)

4.4.4 Liquid Phases - Expressed as weight percent coated on solid support.

4.4.4.1 OV-210, 5%

4.4.4 2 OV-17, 1.5% plus QF-1 or OV-210, 1.95%

4.5 Kuderna-Danish (K-D) Glassware

4.5.1 Snyder Column - three ball (macro) and two ball (micro)

4.5.2 Evaporative Flasks - 250 ml

4.5.3 Receiver Ampuls - 10 ml, graduated

4.5.4 Ampul Stoppers

4.6 Blender - High speed, glass or stainless steel cup.

4.7 Graduated cylinders - 100 and 250 ml.

4.8 Erlenmeyer flasks - 125 ml, 250 ml ground glass ⅝ 24/40

4.9 Microsyringes - 10, 25, 50 and 100 l.

4.10 Pipets - Pasteur, glass disposable (140 mm long X 5 mm ID).

4.11 Separatory Funnels - 60 ml and 2000 ml with Teflon stopcock.

4.12 Glass wool - Filtering grade, acid washed.

4.13 Diazald Kit - Recommended for the generation of diazomethane (available from Aldrich Chemical Co., Cat. #210,025-2).

5. Reagents, Solvents and Standards

5.1 Boron Trifluoride-Methanol-esterification-reagent, 14 percent boron trifluoride by weight.

5.2 N-methyl-N-nitroso-p-toluenesulfonamide (Diazald) - High purity, melting point range 60-62°C. Precursor for the generation of diazomethane (see Appendix IV).

5.3 Potassium Hydroxide Solution - A 37 percent aqueous solution prepared from reagent grade potassium hydroxide pellets and reagent water.

5.4 Sodium Chloride - (ACS) Saturated solution (pre-rinse NaCl with hexane) in distilled water.

5.5 Sodium Hydroxide - (ACS) 10 N in distilled water.

5.6 Sodium Sulfate, Acidified - (ACS) granular sodium sulfate, treated as follows: Add 0.1 ml of conc. sulfuric acid to 100g of sodium sulfate slurried with enough ethyl ether to just cover the solid. Remove the ether with the vacuum. Mix 1 g of the resulting solid with 5 ml of reagent water and ensure the mixture to have a pH below 4. Store at 130°C.

5.7 Sulfuric acid - (ACS) concentrated, Sp. Gr. 1.84.

5.8 Florisil - PR grade (60-100 mesh) purchased activated at 1250°F and stored at 130°C.

5.9 Carbitol (diethylene glycol monoethyl ether).

5.10 Diethyl Ether - Nanograde, redistilled in glass, if necessary.

5.10.1 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.)

5.10.2 Procedures recommended for removal of peroxides are provided with the test strips.

5.11 Benzene Hexane - Nanograde, redistilled in glass, if necessary.

5.12 Pesticide Standards - Acids and Methyl Esters, reference grade.

5.12.1 Stock standard solutions - Dissolve 100 mg of each herbicide in 60 ml ethyl ether; then make to 100 ml with redistilled hexane. Solution contains 1 mg/ml.

5.12.2 Working standard - Pipet 1.0 ml of each stock solution into a single 100 ml volumetric flask. Make to volume with a mixture of ethyl ether and hexane (1:1). Solution contains 10 µg/ml of each standard.

5.12.3 Standard for Chromatography (Diazomethane Procedure) - Pipet 1.0 ml of the working standard into a glass stoppered test tube and evaporate the solvent using a steam bath. Add 2 ml diazomethane to the residue. Let stand 10 minutes with occasional shaking, then allow the solvent to evaporate spontaneously. Dissolve the residue in 200 µl of hexane for gas chromatography.

5.12.4 Standard for Chromatgraphy (Boron Trifluoride Procedure) - Pipet 1.0 ml of the working standard into a glass stoppered test tube. Add 0.5 ml of benzene and evaporate to 0.4 ml using a two-ball Snyder microcolumn and a steam bath. Proceed as in 11.3.1. Esters are then ready for gas chromatography.

6. Calibration

6.1 Gas chromatographic operating conditions are considered acceptable if the response to dicapthon is at least 50% of full scale when ≤ 0.06 ng is injected for electron capture detection and ≤ 100 ng is injected for microcoulometric or electrolytic conductivity detection. For all quantitative measurements, the detector must be operated within its linear response range and the detector noise level should be less than 2% of full scale.

6.2 Standards, prepared from methyl esters of phenoxy acid herbicides calculated as the acid equivalent, are injected frequently as a check on the stability of operating conditions. Gas chromatograms of several chlorophenoxys are shown in Figure 1.

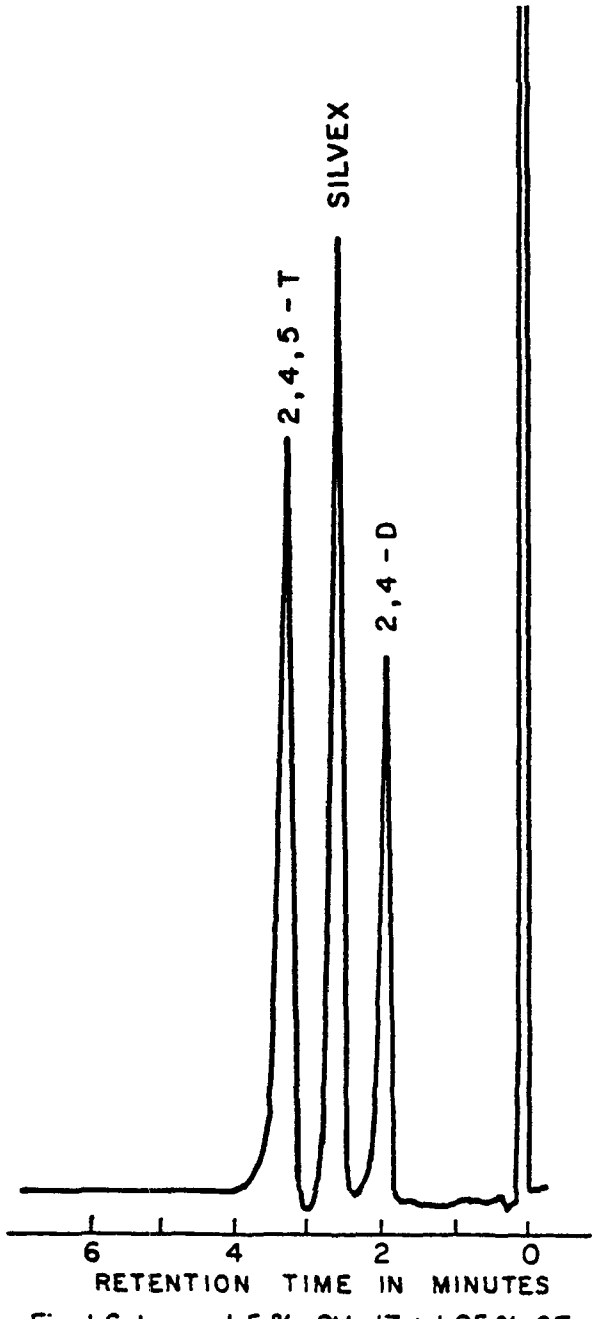

Fig. 1 Column: 1.5 % OV -17 + 1.95 % QF - 1,
Carrier Gas : Argon (5%) / Methane : 70 ml/min.,
Column Temp. 185 C, Detector : Electron Capture .

6.3 The elution order and retention ratios of methyl esters of chlorinated phenoxy acid herbicides are provided in Table 1, as a guide.

7. Quality Control

7.1 Duplicate and spiked sample analyses are recommended as quality control checks. Quality control charts (2) should be developed and used as a check on the analytical system. Quality control check samples and performance evaluation samples should be analyzed on a regular basis.

7.2 Each time a set of samples is extracted, a method blank is determined on a volume of distilled water equivalent to that used to dilute the sample.

8. Sample Preparation

8.1 The sample size taken for analysis is dependent on the type of sample and the sensitivity required for the purpose at hand. Background information on the pesticide levels previously detected at a given sampling site will assist in determining the sample size required, as well as the final volume to which the extract needs to be concentrated. A 1-liter sample is usually taken for drinking water and ambient water analysis to provide a detection limit of 0.050 to 0.100 µg/l. One-hundred milliliters is usually adequate to provide a detection limit of 1 µg/l for industrial effluents.

Table 1

RETENTION RATIOS FOR METHYL ESTERS OF SOME CHLORINATED PHENOXY ACID HERBICIDES RELATIVE TO 2,4-D

Liquid Phase[1]	1.5% OV-17 + 1.95% OF-1[2]	5% OV-210
Column Temp.	185°C	185°C
Argon/Methane Carrier Flow	70 ml/min	70 ml/min
Herbicide	RR	RR
dicamba	0.60	0.61
2,4-D	1.00	1.00
silvex	1.34	1.22
2,4,5-T	1.72	1.51
2,4-D (minutes absolute)	2.00	1.62

[1]All columns glass, 180 cm x 4 mm ID, solid support Gas Chrom Q (100/120 mesh)

[2]OV-210 may be substituted

8.2 Quantitatively transfer the proper aliquot of sample from the sample container into a two-liter separatory funnel. If less than 800 ml is analyzed, dilute to one liter with interference free distilled water.

9. Extraction

9.1 Add 150 ml of ether to the sample in the separatory funnel and shake vigorously for one minute.

9.2 Allow the contents to separate for at least ten minutes. After the layers have separated, 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 percent aqueous potassium hydroxide.

9.3 Extract the sample two more times using 50 ml of ether each time, and combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

10. Hydrolysis

10.1 Add 15 ml of distilled water and a small boiling stone to the flask containing the ether extract, and fit the flask with a 3-ball Snyder column. Evaporate the ether on a steam bath and continue heating for a total of 60 minutes.

10.2 Transfer the concentrate to a 60-ml separatory funnel. Extract the basic solution two times with 20 ml of ether and discard the ether layers. The herbicides remain in the aqueous phase.

10.3 Acidify the contents of the separatory funnel by adding 2 ml of cold (4°C) 25 percent sulfuric acid (5.9). Extract the herbicides once with 20 ml of ether and twice with 10 ml of ether. Collect the extracts in a 125-ml Erlenmeyer flask containing about 0.5 g of acidified anhydrous sodium sulfate (5.8). Allow the extract to remain in contact the the sodium sulfate for approximately two hours.

11. Esterification (3,4)

11.1 Transfer the ether extract, through a funnel plugged with glass wool, into a Kuderna-Danish flask equipped with a 10-ml graduated ampul. Use liberal washings of ether. Using a glass rod, crush any caked sodium sulfate during the transfer.

11.1.1 If esterification is to be done with diazomethane, evaporate to approximately 4 ml on a steam bath (do not immerse the ampul in water) and proceed as directed in Section 11.2. Prepare diazomethane as directed in Appendix IV.

11.1.2 If esterification is to be done with boron trifluoride, add 0.5 ml benzene and evaporate to about 5 ml on a steam bath. Remove the ampul from the flask and further concentrate the extract to 0.4 ml using a two-ball Snyder microcolumn and proceed as in 11.3.

11.2 Diazomethane Esterification

11.2.1 Disconnect the ampul from the K-D flask and place in a hood away from steam bath. Adjust volume to 4 ml with

ether, add 2 ml diazomethane, and let stand 10 minutes with occasional swirling.

11.2.2 Rinse inside wall of ampul with several hundred microliters of ethyl ether. Take sample to approximately 2 ml to remove excess diazomethane by allowing solvent to evaporate spontaneously (room temperature.

11.2.3 Dissolve residue in.5 ml of hexane. Analyze by gas chromatography.

11.2.4 If further clean-up of the sample is required, proceed as in 11.3.4 substituting hexane for benzene.

11.3 Boron Trifluoride Esterification

11.3.1 After the benzene solution in the ampul has cooled, add 0.5 ml of borontrifluoride-methanol reagent. Use the two-ball Snyder microcolumn as an air-cooled condenser and hold the contents of the ampul at 50°C for 30 minutes on the steam bath.

11.3.2 Cool and add about 4.5 ml of a neutral 5 percent aqueous sodium sulfate solution so that the benzene-water interface is in the neck of the Kuderna-Danish ampul. Seal the flask with a ground glass stopper and shake vigorously for about one minute. Allow to stand for three minutes for phase separation.

11.3.4 Pipet the solvent layer from the ampul to the top of a small column prepared by plugging a disposable Pasteur

pipet with glass wool and packing with 2.0 cm of sodium sulfate over 1.5 cm of Florisil adsorbent. Collect the eluate in a graduated ampul. Complete the transfer by repeatedly rinsing the ampul with small quantities of benzene and passing the rinses through the column until a final volume of 5.0 ml of eluate is obtained. Analyze by gas chromatography.

12. Calculation of Results

12.1 Determine the methyl ester concentration by using the absolute calibration procedure described below or the relative calibration procedure described in Appendix III.

(1) $$\text{Micrograms/liter} = \frac{(A)\ (B)\ (V_t)}{(V_i)\ (V_s)}$$

$A = \frac{\text{ng standard}}{\text{standard area}}$

B = Sample aliquot area

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

12.2 Molecular weights for the calculation of methyl esters as the acid equivalents.

2,4-D	222.0	Dicamba	221.0
2,4-D methyl ester	236.0	Dicamba methyl ester	236.1
Silvex	269.5	2,4,5-T	255.5
Silvex methyl ester	283.5	2,4,5-T methyl ester	269.5

13. Reporting Results

13.1 Report results in micrograms per liter as the acid equivalent without correction for recovery data. When duplicate and spiked samples are analyzed all data obtained should be reported.

REFERENCES:

1. Goerlitz, D. G., and Lamar, W. L., "Determination of Phenoxy and Herbicides in Water by Electron-Capture and Microcoulometric Gas Chromatography", U. S. Geol. Survey Water-Supply Paper 1817-C (1967).

2. "Handbook for Analytical Quality Control in Water and Wastewater Laboratories" (1972), U. S. Environmental Protection Agency, National Environmental Research Center, Analytical Quality Control Laboratory, Cincinnati, Ohio, 45268.

3. Metcalf, L. D. and Schmitz, A. A., "The Rapid Preparation of Fatty Acid Esters for Gas Chromatographic Analysis", Analytical Chemistry, 33, 363 (1961).

4. Schlenk, H. and Gellerman, J. L., "Esterification of Fatty Acids with Diazomethane on a Small Scale", Analytical Chemistry, 32, 1412 (1960).

METHOD FOR VOLATILE CHLORINATED ORGANIC COMPOUNDS IN WATER AND WASTEWATERS

1. Scope and Application

1.1 This method covers the determination of various chlorinated organic compounds in water and wastewater.

1.2 The following chlorinated organic compounds may be determined individually by this method:

Parameter	Storet No.
Benzylchloride	---
Carbon tetrachloride	32102
Chlorobenzene	34301
Chloroform	32106
Epichlorohydrin	---
Methylene Chloride	34423
1,1,2,2-Tetrachloroethane	---
Tetrachloroethylene	34475
1,2,4-Trichlorobenzene	---
1,1,2-Trichloroethane	---

2. Summary

2.1 If the sample is turbid, it is initially centrifuged or filtered through a fiber glass filter in order to remove suspended matter. A three to ten microliter aliquot of the sample is injected into the gas chromatograph equipped with a halogen specific detector. The resulting chromatogram is used to identify and quantitate specific components in the sample. Results are reported in micrograms per liter. Confirmation of qualitative identifications are made using two or more dissimilar columns.

3. Interferences

3.1 The use of a halogen specific detector minimizes the possibility of interference from compounds not containing chlorine, bromine, or iodine. Compounds containing bromine or iodine will interfere with the determination of organochlorine compounds. The use of two dissimilar chromatographic columns helps to eliminate this interference and, in addition, this procedure helps to verify all qualitative identifications. When concentrations are sufficiently high, unequivocal identifications can be made using infrared or mass spectroscopy. Though non-specific, the flame ionization detector may be used for known systems where interferences are not a problem.

3.2 Ghosting is usually attributed to the history of the chromatographic system. Each time a sample is injected, small amounts of various compounds are adsorbed on active sites in the inlet and at the head of the column. Subsequent injections of water tend to steam clean these sites resulting in non-representative peaks or displacement of the baseline. This phenomenon normally occurs when an analysis of a series of highly concentrated samples is followed by a low level analysis. The system should be checked for ghost peaks prior to each quantitative analysis by injecting distilled water in a manner identical to the sample analysis (1). If excessive ghosting occurs, the following corrective measures should be applied, as required, in the order listed:

1) Multiple flushes with distilled water

2) Clean or replace the glass injector liner

3) Replace the chromatographic column.

4. Apparatus and Materials

4.1 Gas Chromatograph - Equipped with programmed oven temperature controls and glass-lined injection port. The oven should be equipped with a column exit port and heated transfer line for convenient attachment to the halogen specific detector.

4.2 Detector Options:

4.2.1 Microcoulometric Titration

4.2.2 Electrolytic Conductivity

4.2.3 Flame Ionization

4.3 Recorder - Potentiometric strip chart recorder (10 in) compatible with the detector.

4.4 Syringes - 1 µl, 10 µl, and 50 µl.

4.5 BOD type bottle or 40 ml screw cap vials sealed with Teflon faced silicone septa.

4.6 Volumetric Flasks - 500 ml, 1000 ml.

4.7 Syringe - Hypodermic Lur-lock type (30 ml).

4.8 Filter glass fiber filter - Type A (13 mm).

4.9 Filter holder - Swinny-type hypodermic adapter (13 mm).

4.10 Glass stoppered ampuls - 10 ml

4.11 Chromatographic columns

4.11.1 Moderately-Polar Column - 23 ft x 0.1 in ID x 0.125 in OD stainless steel column #304 packed with 5% Carbowax 20 M on Chromosorb-W (60-80 mesh).

4.11.2 Highly-Polar Column - 23 ft x 0.1 in ID x 0.125 in OD stainless steel #304 packed with 5% 1,2,3-Tris-(2-cyano-ethoxy) propane on Chromosorb-W (60-80 mesh).

4.11.3 Porous Polymer Column - 6 ft x 0.1 in ID x 0.125 in OD stainless steel #304 packed with Chromosorb-101 (60-80 mesh).

4.11.4 Carbopack Column - 8 ft x 0.1 in ID x 0.125 in OD stainless steel #304 packed with Carbopack-C (80-100 mesh) + 0.2% Carbowax 1500.

5. Reagents

5.1 Chlorinated hydrocarbon reference standards

5.1.1 Prepare standard mixtures in volumetric flasks using contaminant-free distilled water as solvent. Add a known amount of the chlorinated compounds with a microliter syringe. Calculate the concentration of each component as follows:

$$mg/l = (\text{Density of Compound})(\mu l \text{ injected})\left(\frac{1000}{(\text{Dilution Volume (ml)})}\right)$$

6. Quality Control

6.1 Duplicate quantitative analysis on dissimilar columns should be performed. The duplicate quantitative data should agree within experimental error (±6 percent). If not, analysis on a third dissimilar column should be performed. Spiked sample analyses should be routinely performed to insure the integrity of the method.

7. Selection Gas Chromatographic Column

7.1 No single column can efficiently resolve all chlorinated hydrocarbons. Therefore, a specific column must be selected to perform a given analysis. Columns providing only partially or non-resolved peaks are useful only for confirmatory identifications. If the qualitative nature of the sample is known, an efficient column selection can be made by reviewing the literature (2). In doing this, one must remember that injection of large volumes of water can cause two serious problems not normally noted using common gas chromatographic techniques:

1) Water can cause early column failure due to liquid phase displacement.

2) Water passing through the column causes retention times and orders to change when compared to common sample solvent media, i.e., hexane or air.

For these reasons, column life and the separations obtained by direct aqueous injection may not be identical to those suggested in literature.

8. Sample Collection and Handling

8.1 The sample containers should have a total volume in excess of 25 to 40 ml, although larger narrow-mouth bottles may be used.

8.1.1 Narrow mouth screw cap bottles with the TFE fluorocarbon face silicone septa cap liners are strongly recommended. Crimp-seal serum vials with TFE fluorocarbon faced septa or

ground glass stoppered bottles are acceptable if the seal is properly made and maintained during shipment.

8.2 Sample Bottle Preparation

8.2.1 Wash all sample bottles and TFE seals in detergent. Rinse with tap water and finally with distilled water.

8.2.2 Allow the bottles and seals to air dry at room temperature.

8.2.3 Place the bottle in a 200°C oven for one hour, then allow to cool in an area known to be free of organics.

8.2.4 When cool, seal the bottles using the TFE seals that will be used for sealing the samples.

8.3 The sample is best preserved by protecting it from phase separation. Since the majority of the chlorinated solvents are volatile and relatively insoluble in water, it is important that the sample bottle be filled completely to minimize air space over the sample. Acidification will minimize the formation of nonvolatile salts formed from chloroorganic acids and certain chlorophenols. However, it may interfere with the detection of acid degradable compounds such as chloroesters. Therefore, the sample history must be known before any chemical or physical preservation steps can be applied. To insure sample integrity, it is best to analyze the sample within 1 hour of collection.

8.4 Collect all samples in duplicate.

8.5 Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is filled.

8.6 Seal the bottles so that no air bubbles are entrapped in it.

8.7 Maintain the hermetic seal on the sample bottle until analysis.

8.8 Sampling from a water tap.

8.8.1 Turn on water and allow the system to flush. When the temperature of the water has stabilized, adjust the flow to about 500-ml/minute and collect duplicate samples from the flowing stream.

8.9 Sampling from an open body of water.

8.9.1 Fill a 1-quart wide-mouth bottle with sample from a representative area. Carefully fill duplicate 25 to 40 ml-sample bottles from the 1-quart bottle.

9. Sample Preparation

9.1 If the sample is turbid, it should be filtered or centrifuged to prevent syringe plugging or excessive ghosting problems. Filtering the sample is accomplished by filling a 30-ml hypodermic syringe with sample and attaching the Swinny-type hypodermic filter adaptor with a glass fiber filter "Type A" installed. Discard the first 5 ml of sample then collect the filtered sample in a glass stoppered sample filled to the top. (One should occasionally analyze the non-filtered sample to insure that the filtering technique does not adversely affect the sample).

10. Method of Analysis

10.1 Daily, analyze a standard containing 10.0 mg/l of each compound to be analyzed as a quality check sample before any samples are analyzed. Instrument status checks and lower limit of detection estimations based upon response factor calculations at two times the signal to noise ratio are obtained from these data. In

addition, response factor data obtained from this standard can be used to estimate the concentration of the unknowns.

10.2 Analyze the filtered sample of unknown composition by injecting 3 to 10 µl into the gas chromatograph. Record the injection volume and detector sensitivity.

10.3 Prepare a standard mixture consisting of the same compounds in concentrations approximately equal to those detected in the sample. Chromatograph the standard mixture under conditions identical to the unknown.

11. Calculation or Results

11.1 Measure the area of each unknown peak and each reference standard peak as follows:

Area = (Peak Height)(Width of Peak at 1/2 Height)

11.2 Calculate the concentration of each unknown as follows:

$$mg/l = \frac{(\text{Area of Sample peak})(\mu l \text{ of Standard Injected})(\text{Conc'n of Standard})}{(\mu l \text{ of Sample injected})(\text{Area of Standard Peak})}$$

12. Reporting Results

12.1 Report results in mg/l. If a result is negative, report the minimum detectable limit (see 10.1). When duplicate and spiked samples are analyzed, all data obtained should be reported.

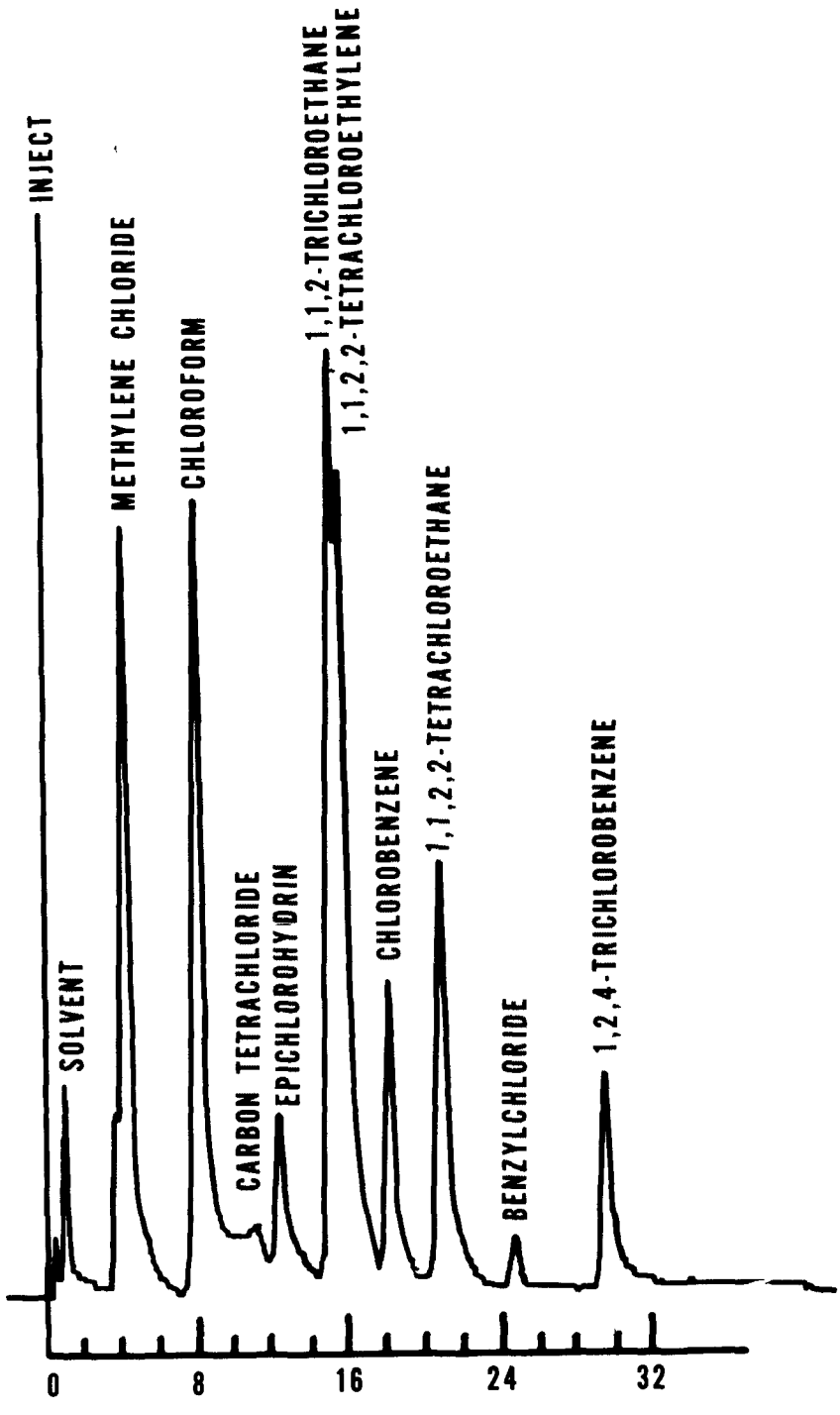

Figure 1. Column: Chromosorb-101, Temperature Program: 125 C for 4 min then 4 C/min up to 280 C., Carrier Gas: Nitrogen at 36 ml/min, Detector: Microcoulometric.

REFERENCES:

1. Dressman, R. C., "Elimination of Memory Peaks Encountered in Aqueous-Injection Gas Chromatography", Journal of Chromatographic Science, 8, 265 (1970).

2. "Gas Chromatography Abstracts", Knapman, C. E. H., Editor, Institute of Petroleum, 61 New Cavendish Street, London W1M8AR, Annually 1958 to date, since 1970, also includes Liquid Chromatography Abstracts.

METHOD FOR PENTACHLOROPHENOL IN WATER AND WASTEWATER

1. Scope and Application

   1.1 This method covers the determination of pentachlorophenol (PCP) in water and wastewater.

2. Summary

   2.1 Pentachlorophenol is extracted from the acidified water sample (pH 3) with toluene, methylated with diazomethane, and analyzed by electron-capture gas chromatography, using the columns listed in the organochlorine pesticide method. (Page 7, this manual)

   2.2 Further identification of pentachlorophenol is made with a mass spectrometer.

3. Interferences

   3.1 Chlorinated pesticides and other high boiling chlorinated organic compounds may interfere with the analysis of PCP.

   3.2 Injections of samples not treated with diazonmethane indicate, to a certain degree, whether interfering substances are present.

4. Precision and Accuracy

   4.1 Single laboratory accuracy and precision reported for this method when analyzing five replicates of tap water spiked with 0.05 to 0.07 µg/l of PCP is as follows:

   Recovery - mean 95.9%, range 88.1 to 100.2%

   Standard Deviation - 6.0%

REFERENCE:

1. "Analysis of Pentachlorophenol Residues in Soil, Water and Fish," Stark, A., Agricultural and Food Chemistry, 17, 871 (July/August 1969).

APPENDIX I

CONSIDERATIONS FOR GLASSWARE AND REAGENTS USED IN ORGANIC ANALYSIS*

1. Glassware

1.1 Cleaning Procedure - It is particularly important that glassware used in trace organic analyses be scrupulously cleaned before initial use as well as after each analysis. The glassware should be cleaned as soon as possible after use, first rinsing with water or the solvent that was last used in it. This should be followed by washing with hot soap water, rinsing with tap water, distilled water, redistilled acetone and finally with pesticide quality hexane. Heavily contaminated glassware may require muffling at 400°C for 15-to 30-minutes. High boiling materials, such as some of the polychlorinated biphenyls (PCBs) may not be eliminated by such heat treatment. NOTE: Volumetric ware should not be muffled. The glassware should be stored immediately after drying to prevent accumulation of dust or other contaminants. Store inverted or cover mouth with foil.

1.2 Calibration - Individual Kuderna-Danish concentrator tubes and/or centrifuge tubes used for final concentration of extracts must be

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*Methods for Organic Pesticides in Water and Wastewater," 1971, Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio, 45268

accurately calibrated at the working volume. This is especially important at volumes below 1 ml. Calibration should be made using a precision microsyringe, recording the volume required to bring the liquid level to the individual graduation marks. Glass A volumetric ware should be used for preparing all standard solutions.

2. Standards, Reagents and Solvents

2.1 Analytical Standards and Other Chemicals - Analytical reference grade standards should be used whenever available. They should be stored according to the manufacturer's instructions. Standards and reagents sensitive to light should be stored in dark bottles and/or in a cool dark place. Those requiring refrigeration should be allowed to come to room temperature before opening. Storing of such standards under nitrogen is advisable.

2.1.1 Stock Standards - Pesticide stock standards solutions should be prepared in 1 µg/µl concentrations by dissolving 0.100-grams of the standard in pesticide-quality hexane or other appropriate solvent (Acetone should not be used since some pesticides degrade on standing in this 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. These standards should be checked frequently for signs of degradation and concentration, especially just prior to preparing working standards from them.

2.1.2 Working Standards - Pesticide working standards are prepared from the stock solutions using a micro syringe preferably equipped with a Chaney adapter. The concentration of the working standards will vary depending on the detection system employed and the level of pesticide in the samples to be analyzed. A typical concentration (0.1 ng/µl) may be prepared by diluting 1 µl of the 1 µg/ul stock to volume in a 10-ml ground glass stoppered volumetric flask. The standard solutions should be transferred to ground glass stoppered reagent bottles. Preparation of a fresh working standard each day will minimize concentration through evaporation of solvent. These standards should be stored in the same manner as the stock solutions.

2.1.3 Identification of Reagents - All stock and working standards should be labeled as follows: name of compound, concentration, date prepared, solvent used, and name of person who prepared it.

2.1.4 Anhydrous sodium sulfate used as a drying agent for solvent extracts should be prewashed with the solvent or solvents that it comes in contact with in order to remove any interferences that may be present.

2.1.5 Glass wool used at the top of the sodium sulfate column must be pre-extracted for about 40-hours in soxhlet using the appropriate solvent.

2.2 Solvents - Organic solvents must be of pesticide quality and demonstrated to be free of interferences in a manner compatible with whatever analytical operation is to be performed. Solvents can be checked by analyzing a volume equivalent to that used in the analysis and concentrated to the minimum final volume. Interferences are noted in terms of gas chromatographic response - relative retention time, peak geometry, peak intensity and width of solvent response. Interferences noted under these conditions can be considered maximum. If necessary, a solvent must be redistilled in glass using a high efficiency distillation system. A 60-cm column packed with 1/8 inch glass helices is effective.

2.2.1 Ethyl Ether - Hexane - It is particularly important that these two solvents, used for extraction of organochlorine pesticides from water, be checked for interferences just prior to use. Ethyl ether, in particular, can produce troublesome interferences. (NOTE: The formation of peroxides in ethyl ether creates a potential explosion hazard. Therefore it must be checked for peroxides before use.) It is recommended that the solvents be mixed just prior to use and only in the amount required for immediate use since build-up of interferences often occurs on standing.

2.2.2 The great sensitivity of the electron capture detector requires that all solvents used for the analysis be of pesticide quality. Even these solvents sometimes require

redistillation in an all glass system prior to use. The quality of the solvents may vary from lot to lot and even within the same lot, so that each bottle of solvent must be checked before use.

APPENDIX II

STANDARDIZATION OF FLORISIL COLUMN BY WEIGHT ADJUSTMENT BASED ON ADSORPTION OF LAURIC ACID

1. Scope

   1.1 A rapid method for determining adsorptive capacity of Florisil is based on adsorption of lauric acid from hexane solution. An excess of lauric acid is used and amount not adsorbed is measured by alkali titration. Weight of lauric acid adsorbed is used to calculate, by simple proportion, equivalent quantities of Florisil for batches having different adsorptive capacities.

2. Apparatus

   2.1 Buret -- 25 ml with 1/10 ml graduations.

   2.2 Erlenmeyer flasks -- 125 ml narrow mouth and 25 ml, glass stoppered.

   2.3 Pipet -- 10 and 20 ml transfer.

   2.4 Volumetric flasks -- 500 ml.

3. Reagents and Solvents

   3.1 Alcohol, ethyl. -- USP or absolute, neutralized to phenolphthalein.

   3.2 Hexane -- Distilled from all glass apparatus.

   3.3 Lauric acid -- Purified, CP.

3.4 Lauric acid solution - Transfer 10.000 g lauric acid to 500 ml volumetric flask, dissolve in hexane, and dilute to 500 ml (1 ml = 20 mg).

3.5 Phenolphthalein Indicator - Dissolve 1 g in alcohol and dilute to 100 ml.

3.6 Sodium hydroxide - Dissolve 20 g NaOH (pellets, reagent grade) in water and dilute to 500 ml (1N). Dilute 25 ml 1N NaOH to 500 ml with water (0.05N). Standardize as follows: Weigh 100-200 mg lauric acid into 1250 ml Erlenmeyer flask. Add 50 ml neutralized ethyl alcohol and 3 drops phenolphthalein indicator; titrate to permanent end point. Calculate mg lauric acid/ml 0.05 N NaOH (about 10 mg/ml).

4. Procedure

4.1 Transfer 2.000 g Florisil to 25 ml glass stoppered Erlenmeyer flasks. Cover loosely with aluminum foil and heat overnight at 130°C. Stopper, cool to room temperature, add 20.0 ml lauric acid solution (400 mg), stopper, and shake occasionally for 15 min. Let adsorbent settle and pipet 10.0 ml of supernatant into 125 ml Erlenmeyer flask. Avoid inclusion of any Florisil.

4.2 Add 50-ml neutral alcohol and 3 drops indicator solution; titrate with 0.05N to a permanent end point.

5. Calculation of Lauric Acid Value and Adjustment of Column Weight

5.1 Calculate amount of lauric acid adsorbed on Florisil as follows:

Lauric Acid value = mg lauric acid/g Florisil = 200 - (ml required for titration X mg lauric acid/ml 0.05N NaOH).

5.2 To obtain an equivalent quantity of any batch of Florisil, divide 110 by lauric acid value for that batch and multiply by 20 g. Verify proper elution of pesticides by 6.

6. Test for Proper Elution Pattern and Recovery of Pesticides

6.1 Prepare a test mixture containing aldrin, heptachlor epoxide, p,p'-DDE, dieldrin, Parathion and malathion. Dieldrin and Parathion should elute in the 15% eluate; all but a trace of malathion in the 50% eluate and others in the 6% eluate.

7. References

7.1 "Pesticide Analytical Manual," U.S. Department of Health, Education and Welfare, Food and Drug Administration, Washington, D.C.

7.2 Mills, P.A., "Variation of Florisil Activity: Simple Method for Measuring Adsorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29 (1968).

APPENDIX III

CHROMATOGRAPHIC CALIBRATION TECHNIQUE

Relative Calibration (Internal Standardization):

A relative calibration curve is prepared by simultaneously chromatographing mixtures of the previously identified sample constituent and a reference standard in known weight ratios and plotting the weight ratios against area ratios. An accurately known amount of the reference material is then added to the sample and the mixture chromatographed. The area ratios are calculated and the weight ratio is read from the curve. Since the amount of reference material added is known, the amount of the sample consitituent can be calculated as follows:

$$\text{micrograms/liter} = \frac{Rw \times Ws}{Vs}$$

Rw = Weight ratio of component to standard obtained from calibration curve

Ws = Weight of internal standard added to sample in nanograms

Vs = Volume of sample in milliliters

Using this method, injection volumes need not be accurately measured the detector response need not remain constant since changes in response will not alter the ratio. This method is preferred when the internal standard meets the following conditions:

a) well-resolved from other peaks

b) elutes close to peaks of interest

c) approximates concentration of unknown

d) structurally similar to unknown.

"Methods for Organic Pesticides in Water and Wastewater," U.S. Environmental Protection Agency, National Environmental Research Center, Cincinnati, Ohio 45268

APPENDIX IV

PREPARATION OF DIAZOMETHANE IN ETHER

1. Scope

   1.1 Diazomethane is prepared by reaction of Carbitol and Diazald in the presence of KOH. Solutions of diazomethane decompose rapidly in the presence of solid material such as copper powder, calcium chloride, boiling stones, etc. These solid materials cause solid polymethylene and nitrogen gas to form.

2. Apparatus

   2.1 Distilling flask with condenser, 125 ml, long neck with dropping funnel.

   2.2 Erlenmeyer flasks - 500 ml and 125 ml.

   2.3 Water bath.

3. Reagents and Solvents

   3.1 Ether

   3.2 Potassium hydroxide pellets.

   3.3 Carbitol (diethylene glycol monoethyl ether).

   3.4 Diazald in ether. Dissolve 21.5 g of Diazald in 140 ml ether.

4. Procedure

   4.1 Use a well-ventilated hood and cork stoppers for all connections. Fit a 125-ml long-neck distilling flask with a dropping funnel and an efficient condenser set downward for distillation. Connect the condenser to two receiving flasks in a series - a 500-ml Erlenmeyer

followed by a 125-ml Erlenmeyer containing 30 ml ether. The inlet to the 125-ml Erlenmeyer should dip below the ether. Cool both receivers to 0°C. As a water bath for the distilling flask, set up a 2-liter beaker on a stirplate (hot plate and stirrer), maintaining temperature at 70°C.

4.2 Dissolve 6-g KOH in 10 ml water in the distilling flask (no heat). Ad 35 ml Carbitol (diethylene glycol monoethyl ether), stirring bar, and another 10 ml ether. Connect the distilling flask to the condenser and immerse distilling flask in water bath. By means of the dropping funnel, add a solution of 21.5 g Diazald in 140 ml ether over a period of 20 minutes. After distillation is apparently complete, add another 20 ml ether and continue distilling until distillate is colorless. Combine the contents of the two receivers in a glass bottle (WITHOUT ground glass neck), stopper with cork, and freeze overnight. Decant the diazomethane from the ice crystals into a glass bottle, stopper with cork, and store in freezer until ready for use. The final solution may be stored up to six months without marked deterioration. The 21.5 g of Diazald reacted in this manner produce about 3 g of Diazomethane.

5. Cautions

5.1 Diazomethane is very toxic. It can explode under certain conditions. The following precautions should be observed.

5.1.1 Use only in well-ventilated hood.

5.1.2 Use safety screen.

5.1.3 Do not pipette solution of diazomethane by mouth.

5.1.4 For pouring solutions of diazomethane, use of gloves is optional.

5.1.5 Do not heat solutions at 100°C (EXPLOSIONS).

5.1.6 Store solutions of gas at low temperatures (freezer compartment of explosion-proof refrigerators).

5.1.7 Avoid ground glass apparatus, glass stirrers and sleeve bearings where grinding may occur (EXPLOSIONS).

5.1.8 Keep solutions away from alkali metals (EXPLOSIONS).

6. Reference

6.1 "Pesticide Analytical Manual," U.S. Department of Health, Education and Welfare, Food and Drug Administration, Washington, D.C.

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APPENDIX IV

GUIDELINES ESTABLISHING TEST PROCEDURES FOR THE ANALYSIS OF POLLUTANTS; PROPOSED REGULATIONS

federal register

Monday
December 3, 1979

Part III

Environmental Protection Agency

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

Appendix I—Gas Chromatographic and HPLC Methods—Methods 601 through 612

Purgeable Halocarbons—Method 601

1. *Scope and Application.*

1.1 This method covers the determination of 29 purgeable halocarbons. The following parameters may be determined by this method:

Parameter	STORET No.
Bromoform	32104
Bromodichloromethane	32101
Bromomethane	34413
Carbon tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34105
1,2-Dichlorobenzene	34536
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
Dichlorodifluoromethane	34668
1,1-Dichloroethane	34496
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachloroethene	34475
1,1,1-Trichloroethane	34506
1,1,/2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34488
Vinyl chloride	39175

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed purging chamber. The halocarbons are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a short sorbent tube where the halocarbons are trapped. After the purge is completed, the trap is heated and backflushed with gas to desorb the halocarbons into a gas chromatographic system. A temperature program is used in the GC system to separate the halocarbons before detection with a halide-specific detector.

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the compounds of interest from the interferences.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1. Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

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

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Several complete devices are now

available commercially. The device must meet the following specifications: The unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in Figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including halide-specific detector, column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 μl.

4.6 2-way syringe valve with Luer ends (3 each).

4.7 Syringe—5-ml gas-tight with shut-off valve.

4.8 *Bottle—15-ml screw-cap, with* Teflon cap liner.

5. *Regents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porus polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh.

5.2.3. Silica gel—(35/60 mesh)—Davison, grade–15 or equivalent.

5.2.4 Coconut charcoal 6/10 mesh Barnaby Chaney, CA–580–26 lot # M–2649 or equivalent.

5.3 Activated carbon—Filtrasorb–200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge ahd trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of

5.4.2 A water purfication system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90° C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle and seal with a Teflon line septum and cap.

5.5 Stock standards—Prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—Using a 100 μl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

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

5.5.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards weekly for the six gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standard each month.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in methyl alcohol that contain the compounds of interest, either singly or mixed together. The standards shoud be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the analytical system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of standard in methyl alcohol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 8. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978) before reliable sample analysis may begin.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and blank with surrogate halocarbons. A combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane is recommended to encompass the boiling range covered by this method. From stock standard solutions prepared as above, add a volume to give 1000 μg of each surrogate to 45 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume (20 ng/μl). Dose 5.0 μl of this surrogate spiking solution

directly into the 5 ml syringe with every sample and reference standard analyzed. Prepare a fresh surrogate spiking solution on a weekly basis.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume in excess of 40 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2. The samples must be iced or refrigerated from the time of collection until extraction. If the sample contains free or combined chlorine, add sodium thiosulfate preservative (10 mg/40 ml will suffice for up to 5 ppm Cl_2) to the empty sample bottles just prior to shipping to the sampling site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 14 days of collection.

9. *Sample Extraction and Gas Chromatograph.*

9.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the samples volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 ul of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.4 Close both valves and purge the sample for 11.0 ± .05 minutes.

9.5 After the 11 minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while back-flushing the trap with an inert gas between 20 and 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or sub/ambient, if problems persist) instead of the initial program temperature of 45°C.

9.6 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5 ml flushes of organic-free water.

9.7 After desorbing the sample for approximately four minutes recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool the trap is ready for the next sample.

9.8 Table 1 summarizes some recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by column 1 is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentration levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (μg/l) vs. peak height or area units.

10.2 Reports results in micrograms per liter. When duplicate and spiked samples are samples are analyzed, all data obtained should be reported.

11. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an inter-laboratory method study to determine the accuracy and precision of this test procedure.

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Table 1—*Organohalides Tested Using Purge and Trap Method*

Compound	Retention time (min.)		Detection limit [1]
	Col. 1 [2]	Col. 2 [3]	μg/l
Chloromethane	1.50	5.28	0.0008
Bromomethane	2.17	7.05	0.03
Dichlorodifluoromethane	2.82	(4)	0.03
Vinyl chloride	2.87	5.28	0.01
Chloroethane	3.33	8.68	0.01
Methylene chloride	5.25	10.1	0.01
Trichlorofluoromethane	7.18	(4)	0.01
1,1-Dichloroethene	7.93	7.72	0.006
1,1-Dichloroethane	9.30	12.6	0.004
trans-1; 2-Dichloroethene	10.1	9.38	0.006
Chloroform	10.7	12.1	0.006
1,2-Dichloroethane	11.4	15.4	0.006
1,1,1-Trichloroethane	12.6	13.1	0.005
Carbon tetrachloride	13.0	14.4	0.007
Bromodichloromethane	13.7	14.6	0.006
1,2-Dichloropropane	14.6	16.6	0.004
trans-1,3,-Dichloropropene	15.2	16.6	0.006
Trichloroethene	15.6	13.1	0.005
Dibromochloromethane	16.5	16.6	0.01
1,1,2-Trichloroethane	16.5	16.1	0.006
Cis-1,3-dichloropropene	16.5	16.0	0.006
2-Chloroethylvinyl ether	18.0	(4)	0.06
Bromoform	19.2	19.2	0.02
1,1,2,2-Tetrachloroethane	21.6	(4)	0.006
Tetrachloroethene	21.7	15.0	0.007
Chlorobenzene	24.2	16.9	0.03
1,3-Dichlorobenzene	34.0	22.4	0.04
1,2-Dichlorobenzene	34.9	23.5	0.04
1,4-Dichlorobenzene	35.4	22.3	0.04

[1] Detection limit is calculated from the minimum detectable GC response being equal to five time the GC background noise, using a Hall Model 700-A Detector.

[2] Carbopack B -60/80 mesh coated with 1% SP-1000 packed in an 8 ft × 0.1 in ID stainless steel or glass column with helium carrier gas at 40 ml/min flow rate. Column temperature held at 45°C for 3 min, then programmed at 8°C/min. to 220° then held for 15 min.

[3] Porisil-C 100/120 mesh coated with n-octane packed in a 6 ft × 0.1 in ID stainless steel or glass column with helium carrier gas at 40 ml/min flow rate. Column temperature held at 50°C for 3 min then programmed at 8°C/min to 170° then held for 4 min.

[4] Not determined.

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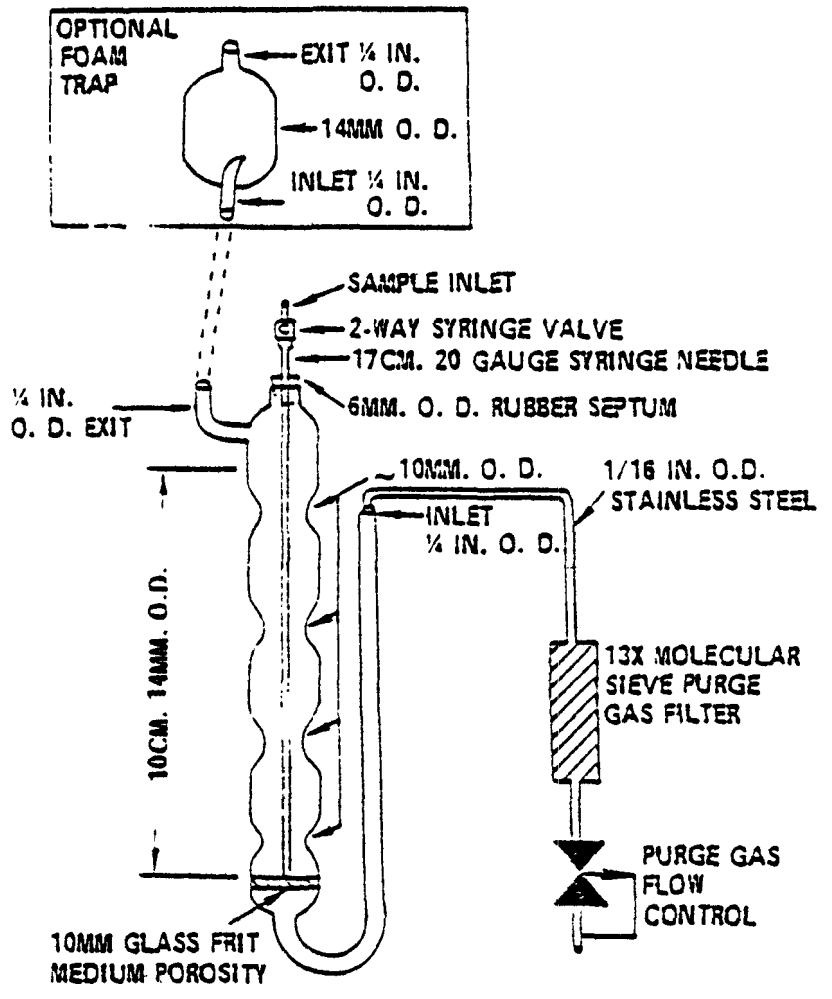

Figure 1. Purging device

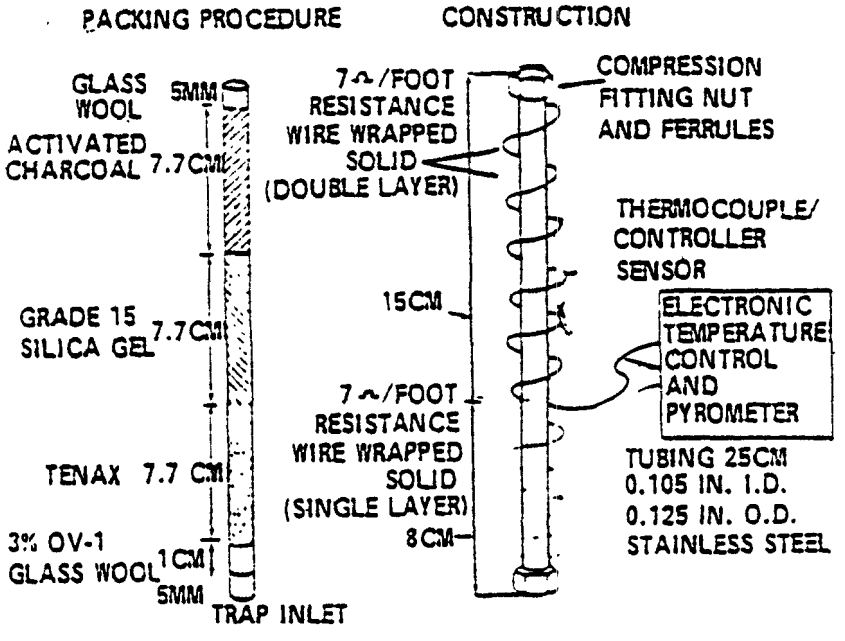

Figure 2. Trap packings and construction to include desorb capability

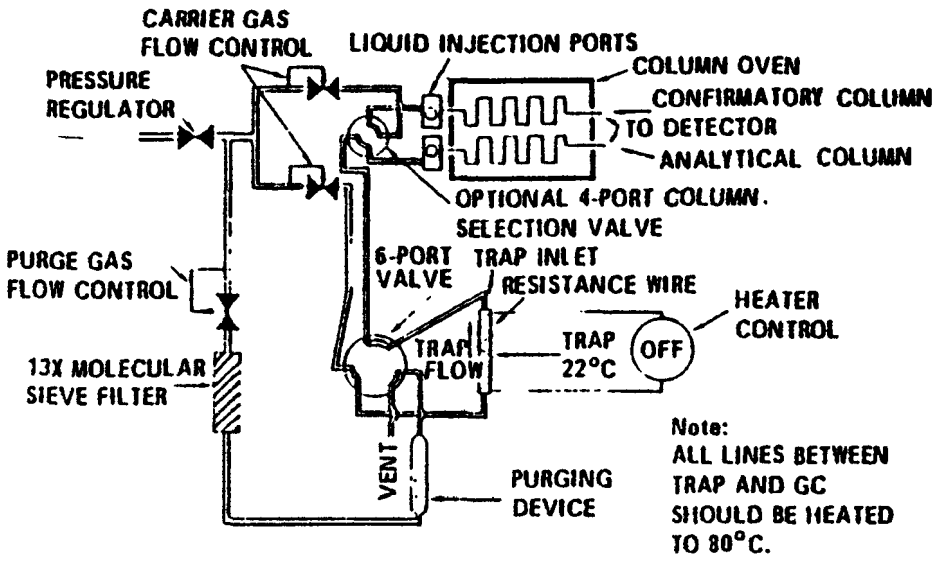

Figure 3. Schematic of purge and trap device - purge mode

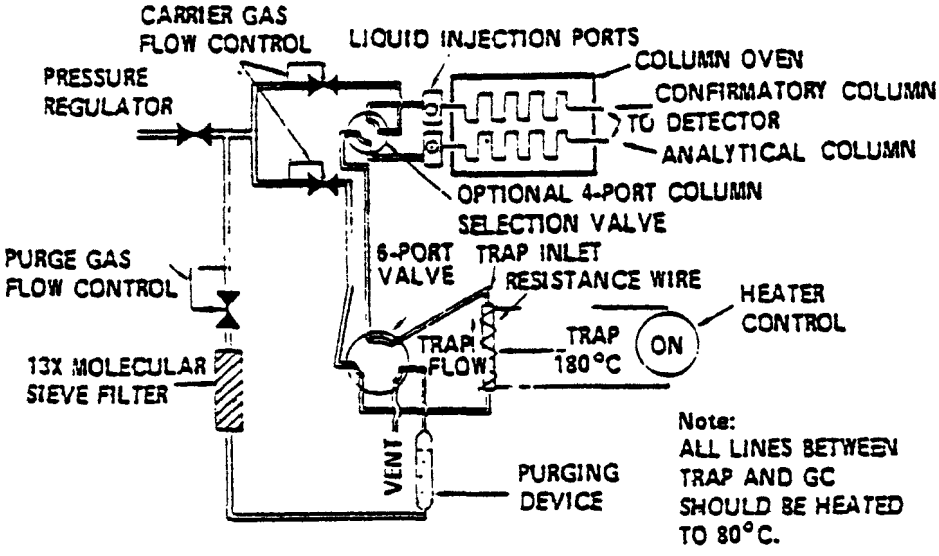

Figure 4. Schematic of purge and trap device - desorb mode

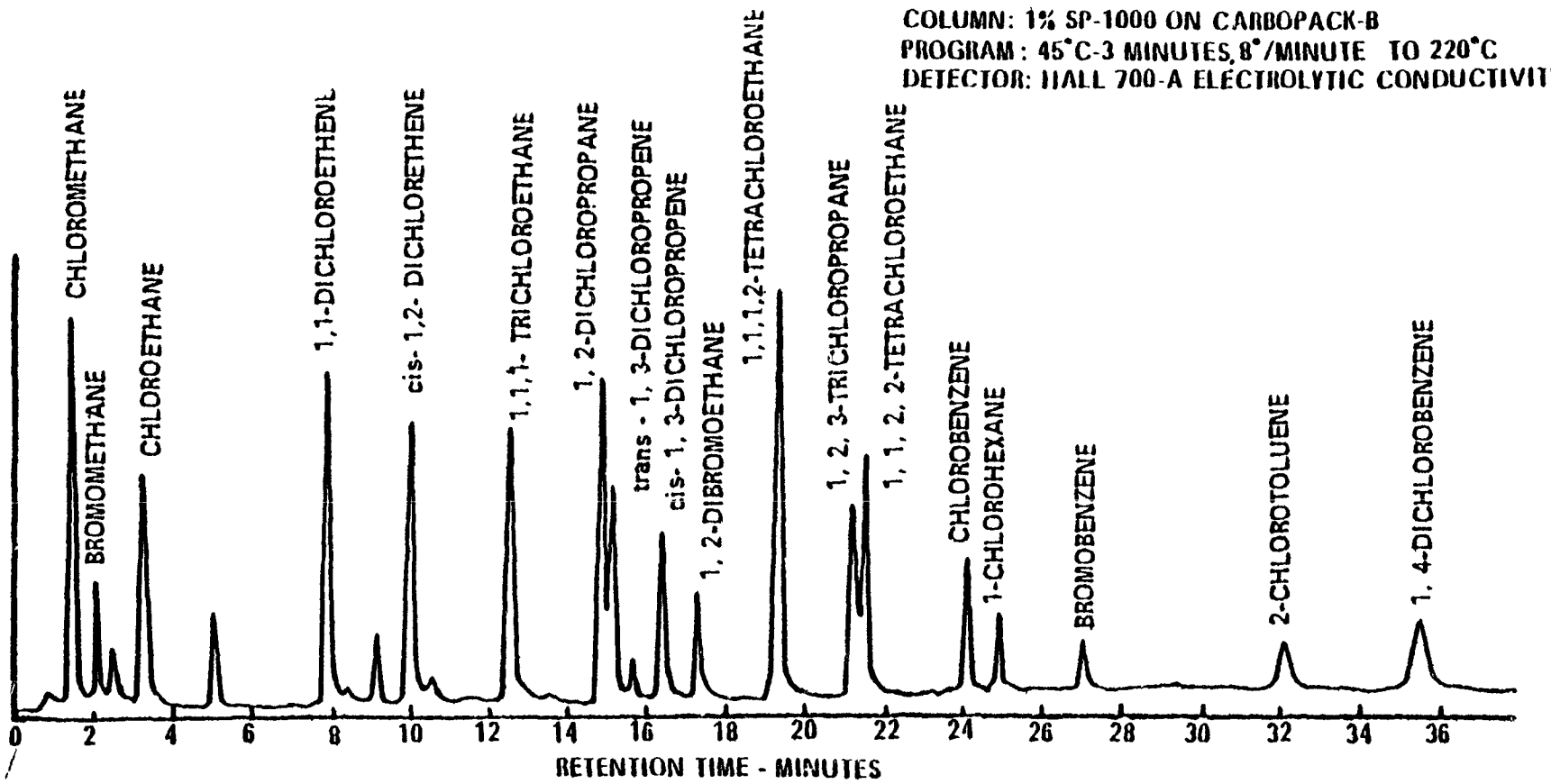

Figure 5. Gas chromatogram of purgeable halocarbons

BILLING CODE 6560-01-C

Purgeable Aromatics—Method 602

1. *Scope and Application.*

1.1 This method covers the determination of various purgeable aromatics. The following parameters may be determined by this method:

Parameter:	Storet No.
Benzene	34030
Chlorobenzene	34301
1,2-Dichlorobenzene	34536
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
Ethylbenzene	34371
Toluene	34010

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed purging chamber. The aromatics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a short sorbent tube where the aromatics are trapped. After the purge is completed, the trap is heated and backflushed with gas to desorb the aromatic compounds into a gas chromatographic system. A temperature program is used in the GC system to separate the aromatics before detection with a photoionization detector.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics through the septum seal into the sample during shipment and storage. A sample blank prepared from organic free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of aromatics, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

4.1.2 Septum-Teflon-faced silicone (Pierce §12722 or equivalent). Detergent wash, rinse, with tap and distilled water, and dry at 105° C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. Several complete devices are available commercially. The device must meet the following specifications: The unit must be completely compatible with the gas chromatograhpic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in Figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories including Model PI–51–02 photoionization detector (h-nu Systems, Inc.), column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hyodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe value with Luer ends (3 each).

4.7 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Reagents.*

5.1 Solium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.2 Three percent OV-1 on Chromosorb-W 60/80 mesh.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water purification system (millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

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

5.5 Stock standards—Prepare stock standard solutions in methyl alcohol using assayed liquids. Because benzene an 1,4-dichlorobenzene are suspected carcinogens, primary dilutions of these compounds should be prepared in a hood.

5.5.1 Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Using a 100 µl syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in mircograms per microliter from the net gain in weight.

5.5.5 Store stock standards at 4°C. All standards must be replaced with fresh standard each month.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in methyl

alcohol that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the analytical system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of standard in methyl alcohol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble th necessary purge and trap device. The Trap must meet the minimum specifications shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180°C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180°C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 8. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978) before reliable sample analysis may begin.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and blank with surrogate compounds (e.g. *aaa*-trifluorotoluene).

8. *Sample Collection, Preservation, and Handling.*

8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to about 2 by adding 1:1 diluted HCl while stirring vigorously. If the sample contains free or combined chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 ml sample bottle in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The samples must be iced or refrigerated from the time of collection until extraction.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.4 Close both valves and purge the sample for 12.0 ± .05 minutes.

9.5 After the 12 minute purge time, disconnect the purge chamber from the trap. Dry the trap by maintaining a flow rate of 40 cc/min dry purge gas for 6 min. Attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap with an inert gas between 20 and 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 50°C.

9.6 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5 ml flushes of organic-free water.

9.7 After desorbing the sample for approximately four minutes recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool the trap is ready for the next sample.

9.8 Table 1 summarized the recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentration levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (μg/l) vs. peak height or area units.

10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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1. Bellar, T. A., and J. J. Lichtenberg, Journal American Water Works Association, Vol. 66, No. 12, Dec. 1974, pp. 739–744.

2. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Proceeding from ASTM Symposium on Measurement of Organic Pollutants in Water and Wastewater, June 1978 (In Press).

3. Bellar, T. A., and J. J. Lichtenberg, "The Determination of Purgeable Aromatic

Compounds in Drinking Waters and Industrial Wastes," (In preparation).

4. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 11—Purgeables and Category 12—Acrolein, Acrylonitrile, and Dichlorodifluoromethane." Report for EPA Contract 68-03-2635 (In preparation).

Table 1.—*Chromatography of Aromatics Using Purge and Trap Method*

Compound	Retention time (min.) Col. 1 [1]	Detection limit µg/l [2]
Benzene	3.33	(3)
Toluene	5.75	(3)
Ethyl benzene	8.25	(3)
Chlorobenzene	9.17	(3)
1,4-Dichlorobenzene	16.8	(3)
1,3-Dichlorobenzene	18.2	(3)
1,2-Dichlorobenzene	25.9	(3)

[1] Supelcoport 100/120 mesh coated with 5% SP-2100 and 1.75% Bentone-34 packed in a 6 ft. x 0.085 in ID stainless steel column with helium carrier gas at 36 cc/min flow rate. Column temperature held at 50°C for 2 min. then programmed at 6°C/min. to 90°C for a final hold.

[2] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, using a h-nu Model PI-51-02 photoionization detector with a 10.2 ev lamp.

[3] Not determined.

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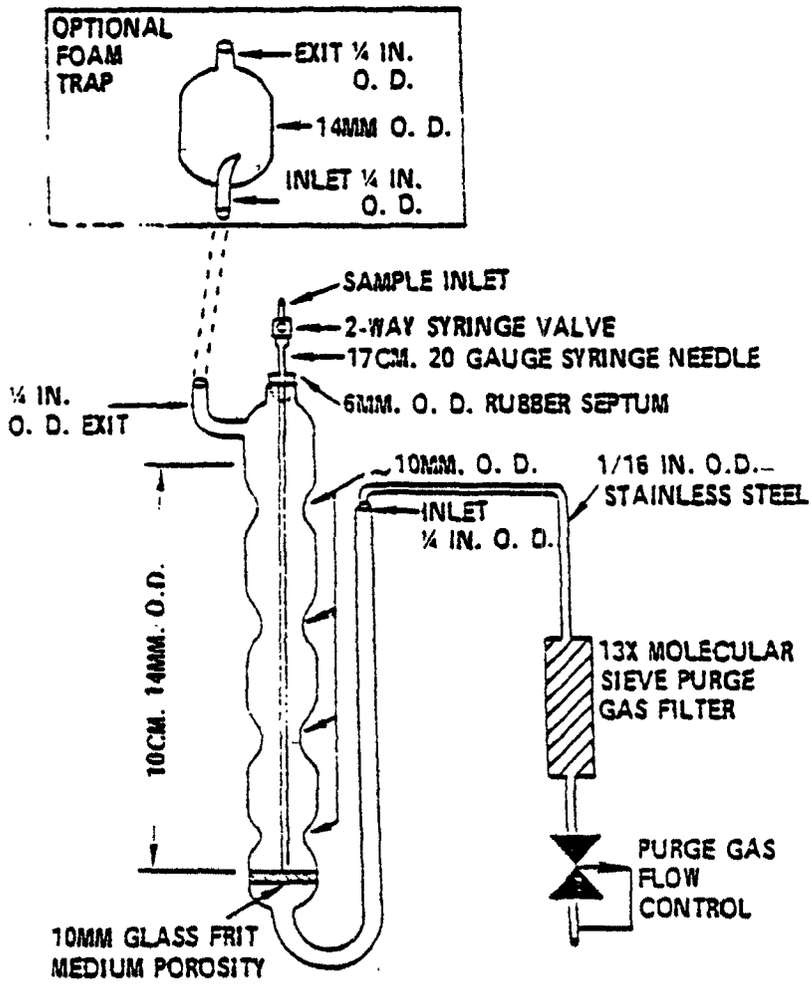

Figure 1. Purging device

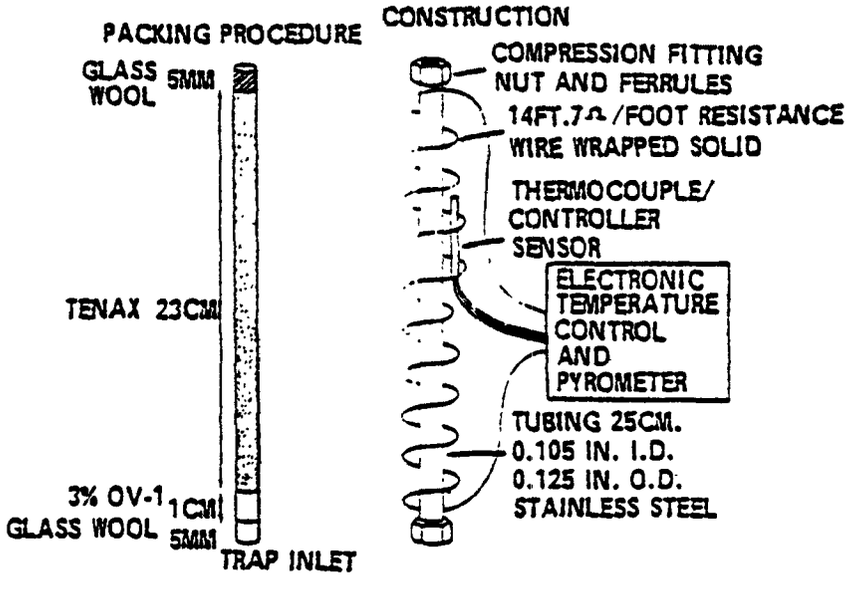

Figure 2. Trap packings and construction to include desorb capability

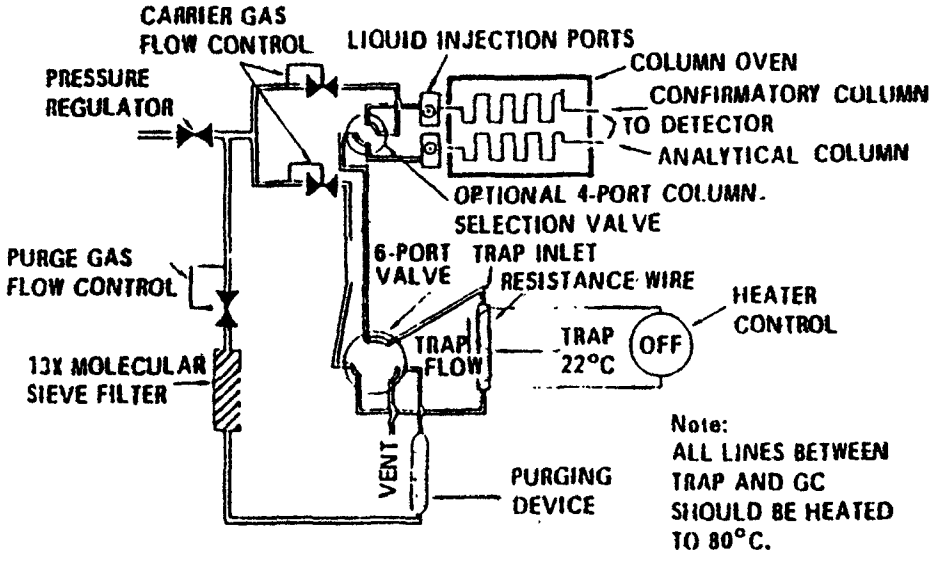

Figure 3. Schematic of purge and trap device - purge mode

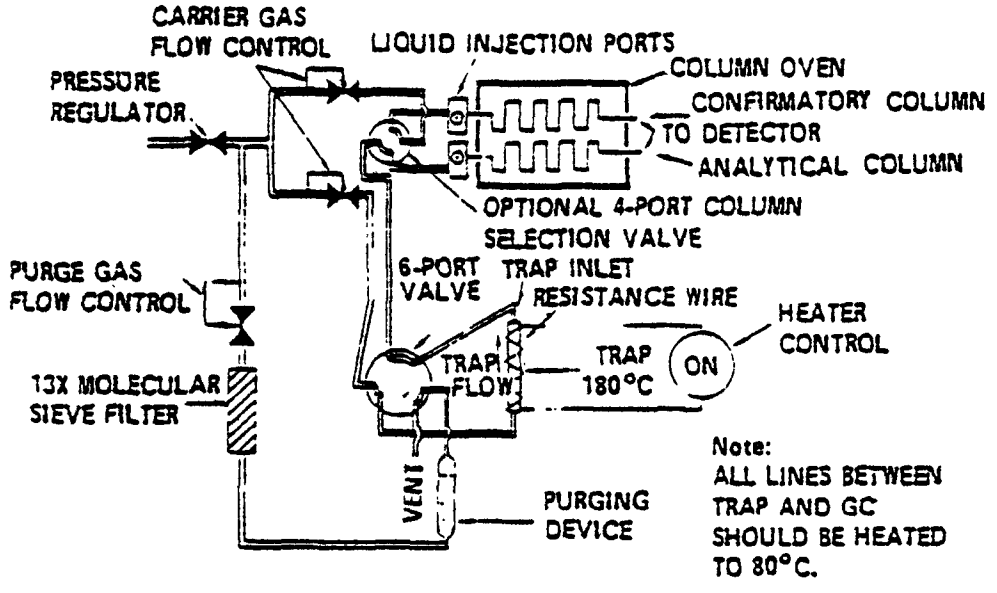

Figure 4. Schematic of purge and trap device - desorb mode

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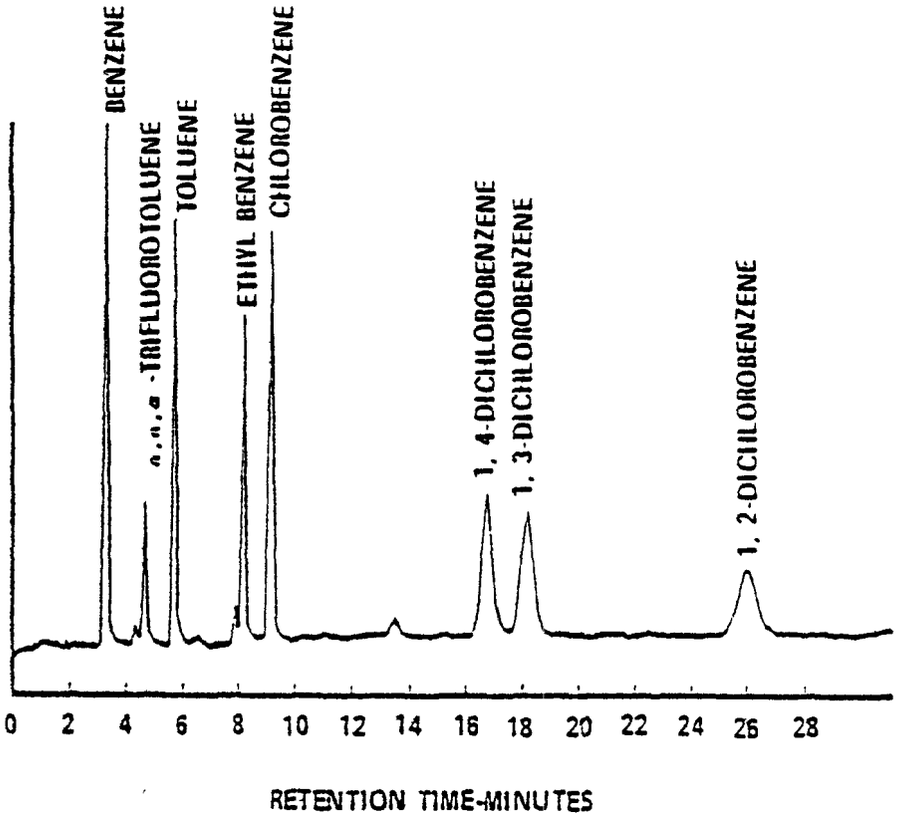

Figure 5. Gas chromatogram of purgeable aromatics

Acrolein and Acrylonitrile—Method 603

1. *Scope and Application.*

1.1 This method covers the determination of acrolein and acrylonitrile. The following parameters may be determined by this method:

Parameter	Storet No.
Acrolein	34210
Acrylonitrile	32415

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 represent sensitivities that can be achieved in wastewaters under optimum operating conditions.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 An inert gas is bubbled through a 5 ml water sample contained in a specially-designed heated purging chamber. Acrolein and acrylonitrile are transferred from the aqueous phase to the vapor phase. The vapor is passed through a short sorbent tube where the compounds are trapped. After the extraction is completed, the trap is heated and backflushed with gas to desorb the compounds into a gas chromatographic system. A temperature program is used in the GC system to separate the compounds before detection with a flame ionization detector.

3. *Interferences.*

3.1 Impurities in the purge gas and organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce the likelihood of this, the purging device and sample syringe should be rinsed out twice between samples with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high organohalide levels it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105° C oven between analyses.

3.4 Interferences are sometimes reduced or eliminated by first purging the water samples for 5 minutes at room temperature in 9.4. Then the purge device is rapidly heated to 85° C and purged as in 9.4. With such a modification, approximately 5 to 10% of the acrylonitrile and a trace of the acrolein in the sample will be lost. Therefore, calibration must be established for the compounds under the conditions of this modified procedure.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry at 105° C before use.

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

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: the purging device, trap, and desorber. The purging device should be equipped for heating in the same manner as the trap (electrically) or with a circulating water jacket. If electrical heating is used the electrical parts must be protected so that water will not drip on the conductors, causing dangerous electrical shock or shorts. All temperature parameters must be carefully controlled. Several complete devices are available commercially although most are not equipped to heat the purging chamber. The device must meet the following specifications: the unit must be completely compatible with the gas chromatographic system; the purging chamber must be designed for a 5 ml volume and be modeled after Figure 1; the dimensions for the sorbant portion of the trap must meet or exceed those in figure 2. Figures 3 and 4 illustrate the complete system in the purge and the desorb mode.

4.3 Gas chromatograph—Analytical system complete with programmable gas chromatograph suitable for on-column injection, equipped with matched columns for dual column analysis and a differential flame ionization detector. A nitrogen specific detector (thermionic or Hall) may be used if only acrylonitrile is to be detected. Required accessories include: column supplies, recorder, and gases. A data system for measuring peak areas is recommended.

4.4 Syringes—5-ml glass hypodermic with luerlok tip (2 each).

4.5 Micro syringes—10, 25, 100 ul.

4.6 2-way syringe valve with Luer ends (3 each).

4.7 Bottle—15-ml screw-cap, with Teflon cap liner.

5. *Reagents.*

5.1 Preservatives

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2. Sulfuric acid—(ACS). Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Trap absorbent—Porous polymer packing, 50/80 mesh chromatographic grade Porapak N.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water.

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water purification system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

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

5.5 Stock standards—Prepare stock standard solutions daily in water using assayed standards. Because of toxicity, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of the materials.

5.5.1 Place about 9.8 ml of water (pH 6.5 to 7.5) into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all water wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the water without contacting the neck of the flask.

5.5.3 Dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15 ml screw-cap bottle with a Teflon cap liner.

5.5.4 Calculate the concentration in micrograms per microliter from the net gain in weight.

6. *Calibration.*

6.1 Using stock standards, prepare secondary dilution standards in water. The standards should be prepared at concentrations such that the aqueous standards prepared in 6.2 will completely bracket the working range of the chromatographic system.

6.2 Using secondary dilution standards, prepare calibration standards by carefully adding 20 ul of stock standard to 100, 500, or 1000 ml of organic-free water.

6.3 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table 1. By injecting secondary dilution standards, establish the sensitivity limit and the linear range of the analytical system for each compound.

6.4 Assemble the necessary purge and trap device. The trap must meet the minimum specifications as shown in Figure 2 to achieve satisfactory results. Condition the trap overnight at 180° C by backflushing with an inert gas flow of at least 20 ml/min. Prior to use, daily condition traps 10 minutes while backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine purging efficiency and also to calculate analytical precision. The purging efficiencies and analytical precision of the analysis of aqueous standards should be 85±5% for acrolein and 98±5% for acrylonitrile.

6.5 By analyzing calibration standards, establish the sensitivity limit and linear range of the entire analytical system for each compound.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water method blank that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram, confirmatory techniques such as mass spectroscopy should be used.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard and blank with surrogate compounds.

8. *Sample Collection, Preservation, and Handling.*

8.1 Collect about 500 ml sample in a clean container. Adjust the pH of the sample to 6.5 to 7.5 by adding 1:1 diluted H_2SO_4 or NaOH while stirring vigorously. If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per part per million of free chlorine per liter of sample. Fill a 40 ml sample bottle and seal the bottle so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

8.3 All samples must be analyzed within 3 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Adjust the helium purge gas flow rate to 20±1 ml/min and the temperature of the purge device to 85°C. Attach the trap inlet to the purging device, and set the device to purge. Open the syringe valve located on the purging device sample introduction needle.

9.2 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the water into the syringe barrel until it oveflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml.

9.3 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.4 Close both valves and purge the sample for 30.0±0.1 minutes. Monitor and control the temperature of the purge device to obtain 85±1°C.

9.5 After the 30-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly hearing the trap to 170°C while backflushing the trap with helium at 45 ml/min for 5 minutes. The backflushing time and gas flow rate must be carefully reproduced from sample to sample. During blackflushing the chromatographic column is held at 100°C. Record GC retention time from the beginning of desorption.

9.6 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5 ml flushes of organic-free water.

9.7 After desorbing the sample for 5 minutes recondition the trap by returning the purge and trap device to the purge mode and begin the GC progrm. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 170°C. After approximately seven minutes turn off the trap heater and open the syringe valve to stop the gas flow through the trap. when cool the trap is ready for the next sample.

9.8 Table 1 summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 5. Calibrate the system daily by analysis of a minimum of three concentrations levels of calibration standards.

10. *Calculations.*

10.1 Determine the concentration of individual compounds directly from calibrations plots of concentration (ug/l) vs. peak height or area units.

10.2 Report results in micrograms per liter. When duplicate and spiked samples are analyzed, all data obtained should be reported.

11. *Accuracy and precision*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

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1. Bellar, T.A., and J.J. Lichtenberg, Journal American Water Works Association, Vol. 66, No. 12, Dec. 1974, pp. 739–744.

2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," Proceeding from ASTM Symposium on Measurement of Organic pollutants in Water and wastewater, June 1978 (In Press).

3. "Development and application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 11–Purgeables and Category 12–Acrolein, Acrylonitrile, and Dichlorodifluoromethane." Report for EPA Contract 68–03–2635 (In preparation).

4. Going, John, et al., "Environmental Monitoring Near Industrial Sites-Acrylonitrile," EPA Report No. 560/6–79–003, 1979.

Table 1.—*Gas Chromatography by Heated Purge and Trap*

Compound [1]	Retention Time (min.)	Detection Limit ug/l [2]
Acrolein	7.6	2
Acrylonitrile	8.9	

[1] Column conditions: Chromosorb 101 80/100 mesh packed in a 6' × ⅛" O.D. stainless steel column with helium carrier gas at 45 ml/min flow rate. Column temperature is held at 100° C for 5 minutes during trap desorption, then programmed at 10 ° C/min to 140 °C and held for 5 minutes.

[2] Detection limit is estimated, based upon the use of a flame ionization detector.

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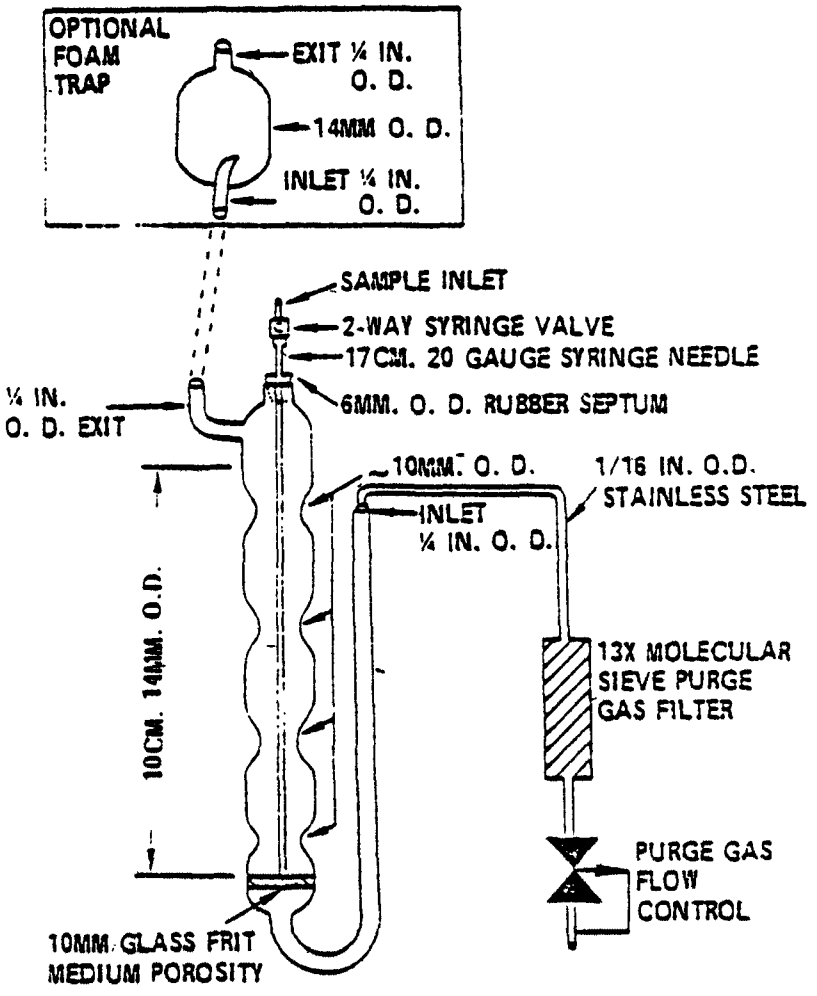

Figure 1. Purging device

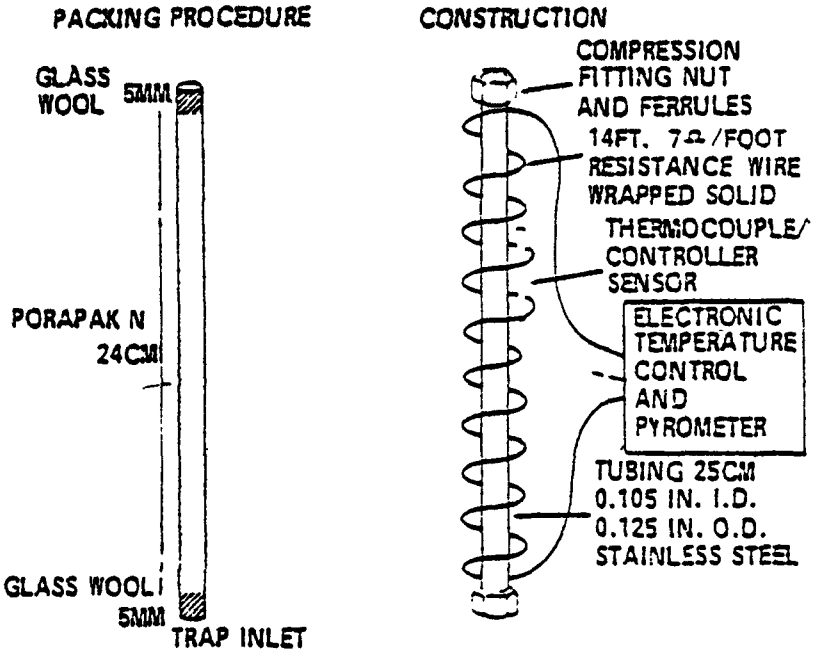

Figure 2. Trap packings and construction to include desorb capability

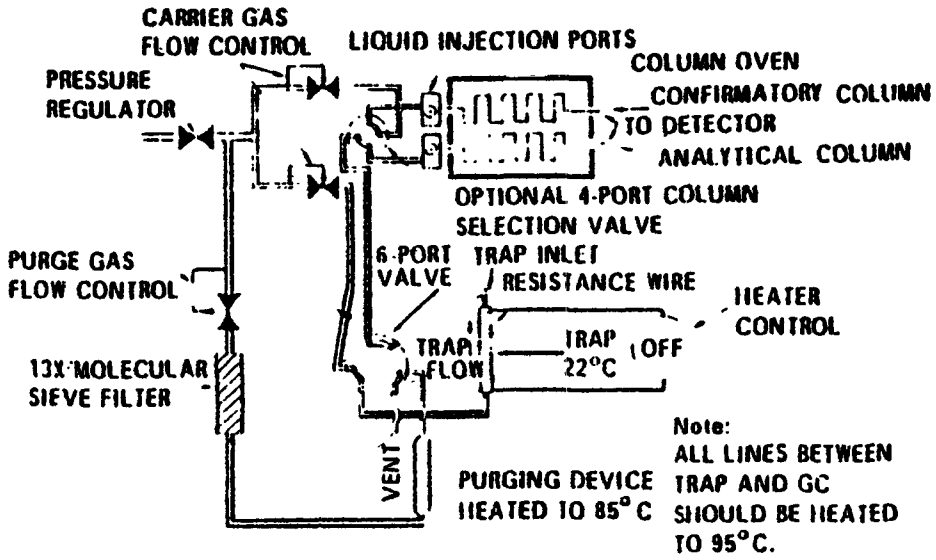

Figure 3. Schematic of purge and trap device - purge mode

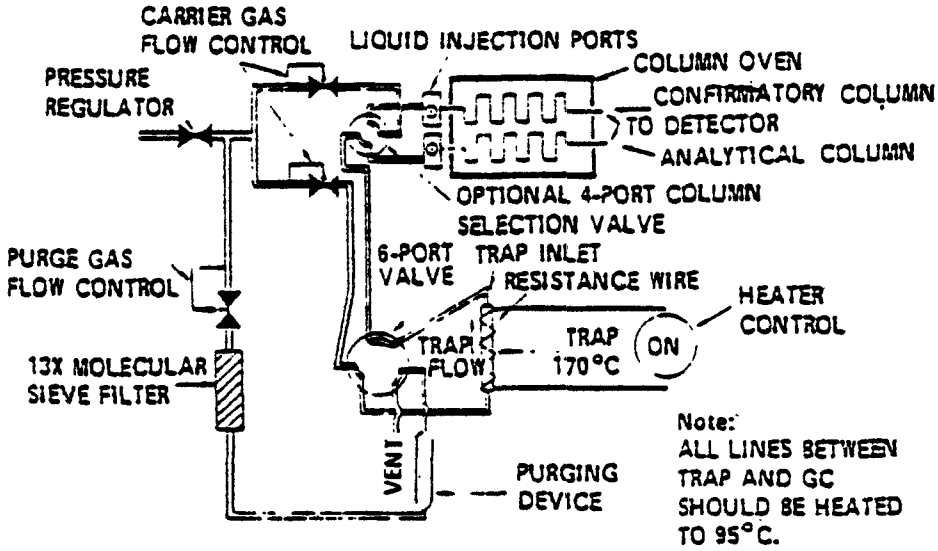

Figure 4. Schematic of purge and trap device - desorb mode

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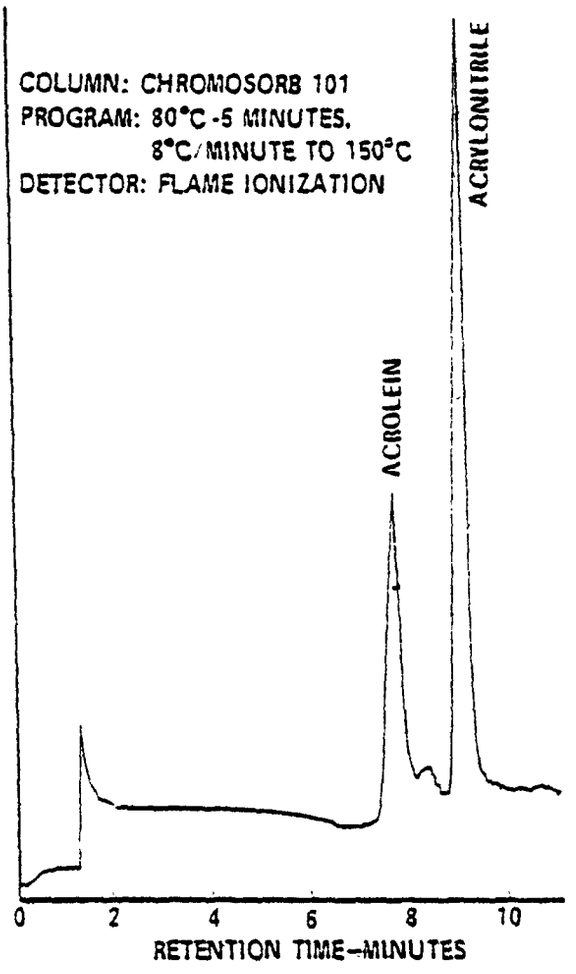

Figure 5. Gas chromatogram of acrolein and acrylonitrile

Phenols—Method 604

1. *Scope and Application.*

1.1 This method covers the determination of various phenolic compounds. The following parameters may be determined by this method:

Parameter	Storet No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39094
Phenol	34694
2,4,6-Trichlorophenol	34621

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters with a flame ionization detector in the absence of interferences. If the derivatization cleanup is required, the sensitivity of the method is 10 μg/1. This concentration represents the minimum amount proven to date to give reproducible and linear response during derivatization.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is acidified and extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Flame ionization gas chromatographic conditions are described which allow for the measurement of the compounds in the extract.

2.2 The method also provides for the preparation of pentafluorobenzylbromide (PFB) derivatives for electron capture gas chromatography with additional cleanup procedures to aid the analyst in the elimination of interferences.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minumum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in this system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID Pyrex chromatographic column with coarse frit.

4.4. Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including flame ionization and electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—10 mm ID by 100 mm length, with Teflon stopcock.

4.8 Reaction vial—20 ml, with Teflon-lined cap.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(1+1) Mix equal volumes of conc. H_2SO_4 (ACS) with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Methylene chloride, acetone, 2-propanol, hexane, toluene—Pesticide quality or equivalent.

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

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Sulfuric acid—(ACS) 1 N in distilled water.

5.6 Potassium carbonate—(ACS) powdered.

5.7 Pentafluorobenzyl bromide (a-Bromopentafluorotoluene)—97% minimum purity.

5.8 1,4,7,10,13,16—Hexaoxacyclooctadecane (18-crown 6)—98% minimum purity.

5.9 Derivatization reagent—Add 1 ml pentafluorobenzyl bromide and 1 gram 18 crown 6 to a 50 ml volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly.

5.10 Silica gel—(ACS) 100/200 mesh, grade 923; activated at 130°C and stored in a sesiccator.

6. *Calibration.*

6.1 Prepare calibration standards for the flame ionization detector that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using the derivatization clean up procedure, the analyst must process a series of calibration standards through the procedure to validate the precision of the derivatization and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. At the sampling location fill the glass container with sample. Add 35 mg of sodium thiosulfate per part per million free chlorine per liter. Adjust the sample pH to approximately 2, as measured by pH paper, using appropriate sulfuric acid

solution or 10N sodium hydroxide. Record the volume of acid used on the sample identification tag so the sample volume can be corrected later.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the sample pH to 12 with sodium hydroxide.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for one minute with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechnical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Discard the methylene chloride layer, and wash the sample with an additional two 60 ml portions of methylene chloride in similar fashion.

9.3 Adjust the aqueous layer to a pH of 1–2 with sulfuric acid.

9.4 Add 60 ml of methylene chloride to the sample and shake for two minutes. Allow the solvent to separate from the sample and collect the methylene chloride in a 250 ml Erlenmeyer flask.

9.5 Add a second 60 ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract the through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.7 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the appartus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling.

9.8 Increase the temperature of the hot water bath to 95–100°C. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of 2-propanol. A 5-ml syringe is recommended for this operation. Attach a micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 ml 2-propanol to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5–10 minutes. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 2.5 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. Add an additional 2 ml of 2-propanol through the top of the micro-Snyder column and resume concentrating as before. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 ml. Stopper the concentrator tube and store in refrigerator, if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with flame ionization gas chromatographic analysis. If the sample requires cleanup, proceed to section 11.

9.9 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. After correction for sulfuric acid preservative, record the sample volume to the nearest 5 ml.

10. *Gas Chromatography-Flame Ionization Detector.*

10.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by one of these columns is shown in Figure 1. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.

10.2 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

10.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

10.4 If the peak area measurement is prevented by the presence of interferences, the phenols must be derivatized and analyzed by electron capture gas chromatography.

11. *Derivatization and Electron Capture Gas Chromatography.*

11.1 Pipet a 1.0 ml aliquot of the 2-propanol solution of standard or sample extract into a glass reaction vial. Add 1.0 ml derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/ml.

11.2 Add about 3 mg of potassium carbonate to the solution and shake gently.

11.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.

11.4 Remove the solution from the hot water bath and allow it to cool.

11.5 Add 10 ml hexane to the reaction vial and shake vigorously for one minute. Add 3.0 ml of distilled, deionized water to the reaction vial and shake for two minutes.

11.6 Decant organic layer into a concentrator tube and cap with a glass stopper.

11.7 Pack a 10 mm ID chromatographic column with 4.0 grams of activated silica gel. After settling the silica gel by tapping the column, add about two grams of anhydrous sodium sulfate to the top.

11.8 Pre-elute the column with 6 ml hexane. Discard the eluate and just prior to exposure of the sulfate layer to air, pipet onto the column 2.0 ml of the hexane solution (11.6) that contains the derivatized sample or standard. Elute the column with 10.0 ml of hexane (Fraction 1) and discard this fraction. Elute the column, in order, with: 10.0 ml 15% toluene in hexane (Fraction 2); 10.0 ml 40% toluene in hexane (Fraction 3); 10.0 ml 75% toluene in hexane (Fraction 4); and 10.0 ml 15% 2-propanol in toluene (Fraction 5). Elution patterns for the phenolic derivatives are shown in Table II. Fractions may be combined as desired, depending upon the specific phenols of interest or level of interferences.

11.9 Analyze the fractions by electron capture gas chromatography.

Table II summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times that should be achieved by this method. Examples of the separation achieved by this column is shown in Figure 2. Calibrate the system daily with a minimum of three aliquots of calibration standards, containing each of the phenols of interest that are derivatized according to the procedure.

11.10 Inject 2–5 μl of the column fractions using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units. If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

12. *Calculations*

12.1 Determine the concentration of individual compounds measured by the flame ionization procedure (without derivatization) according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)\,(B)\,(V_t)}{(V_i)\,(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (μl)

12.2 Determine the concentration of individual compounds measured by the derivatization and electron capture procedure according to the following procedure:

12.2.1 From the concentration of the calibration standards that were derivatized with the samples, calculate the amounts, in nanograms, of underivatized phenols that were added as 2-propanol solution (11.1). From the size of the injection into the electron capture gas chromatograph, determine the nanograms of material (calculated as the underivatized phenol) injected onto the column. Compare the detector responses obtained to develop a calibration factor for the chromatographic system, in nanograms of material per area unit.

12.2.2 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)(10)(D)}{(V_i)(V_s)(C)(E)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit, calculated as underivatized phenol.

B = Peak size in injection of sample extract, in area units.

V_i = Volume of eluate injected (μl)

V_t = Total volume of column eluate (μl)

V_s = Volume of water extracted (ml)

C = Volume of hexane sample solution added to cleanup column, in ml.

D = Total volume of 2-propanol extract after concentration.

E = Volume of 2-propanol extract used for derivatization.

12.3 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3—Chlorinated Hydrocarbons and Category 8—Phenols." Report for EPA Contract 68–03–2625 (In preparation).

Table I.— *Flame Ionization Gas Chromatography of Phenols*

Compound [1]	Retention time	Detection limit (μg/L) [2]
2-Chlorophenol	1.70	2.0
2-Nitrophenol	2.00	2.5
Phenol	3.01	1.4
2,4-Dimethylphenol	4.03	1.7
2,4-Dicloropheno	4.30	2.1
2,4,6-Trichlorophenol	6.05	5.0
4-Chloro-3-methylphenol	7.50	8.3
2,4-Dinitrophenol	10.00	7.0
2-Methyl-4,6-dinitrophenol	10.24	10.0
Pentachlorophenol	12.42	10.0
4-Nitrophenol	24.25	10.0

[1] Column conditions: Supelcoport 80/100 mesh coated with 1% SP–1240 DA in 6 ft long x 2 mm ID glass column with nitrogen carrier gas at 30 ml/min flow rate. Column temperature is 80°C at injection, programmed immediately at 8°C/min to 150°C final temperature.

[2] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final extract volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

Table II.—*Electron Capture Gas Chromatography of PFB Derivatives*

Parent compound [1]	Rentention time (minutes)	Recovery percent by fraction [2]				
		1	2	3	4	5
2-chlorophenol	3.3			90	>1	
2-nitrophenol	9.1				9	90
Phenol	1.8			90	10	
2,4-Dimethyphenol	2.9			95	7	
2,4-Dichlorophenol	5.8			95	>1	
2,4,6-Trichlorophenol	7.0		50	50		
4-Chloro-2-methyphenol	4.8			84	14	
Pentachlorophenol	28.8		75	20		
4-Nitrophenol	14.0				>1	90
(2,4-Dinitrophenol)	[3] 46.9					
(2-Methyl-4,6-dinitrophenol	[3] 36.6					

[1] Column conditions: Chromosorb W-AW-DMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8 m long x 2.0 mm ID glass column with 5% methane/95% argon carrier gas at 30 ml/min flow rate. Column temperature is 200°C.

[2] From: "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Categories 3-Chlorinated Hydrocarbons and Category 8-Phenols."

[3] Retention times included for qualitative information only. The lack of accuracy and precision of the derivatization reaction precludes the use of this approach for quantitative purposes.

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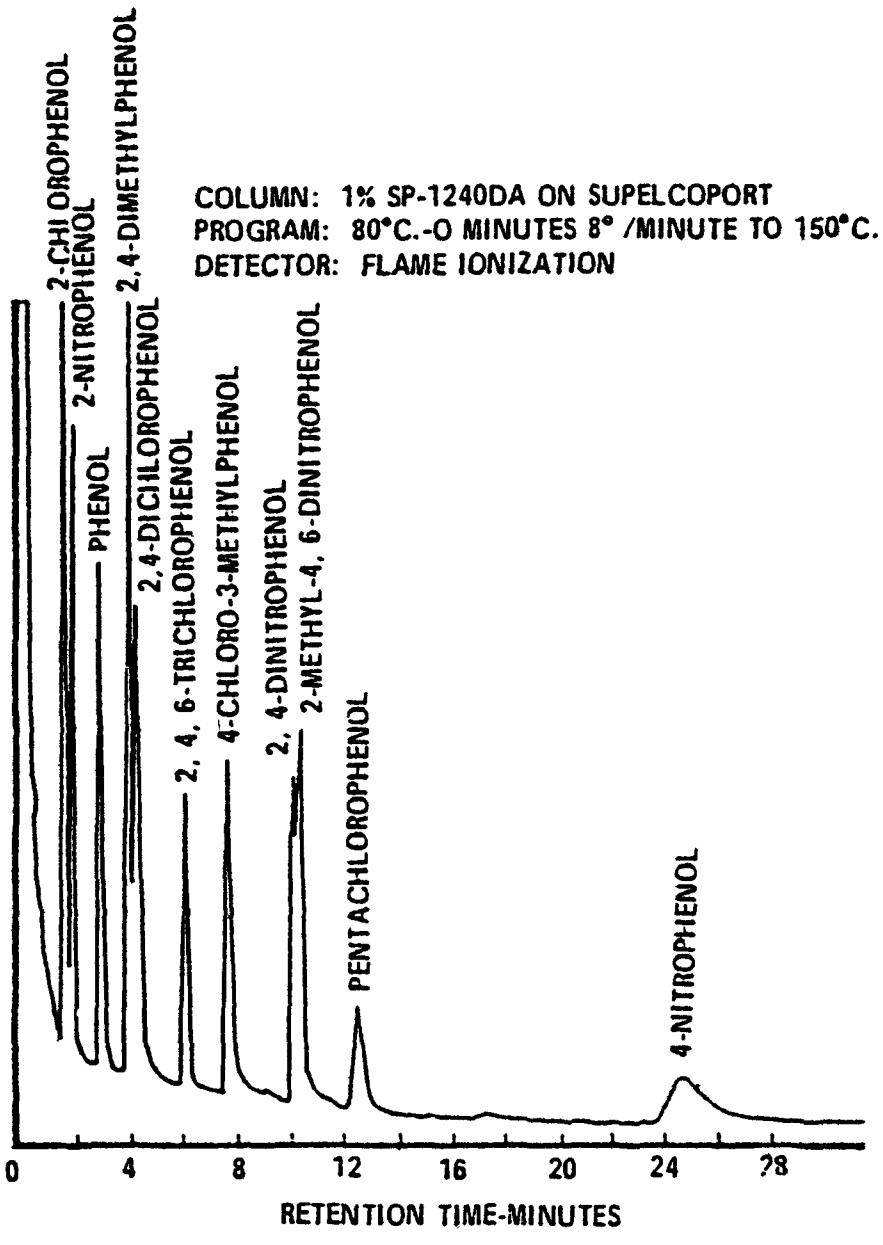

Figure 1. Gas chromatogram of phenols

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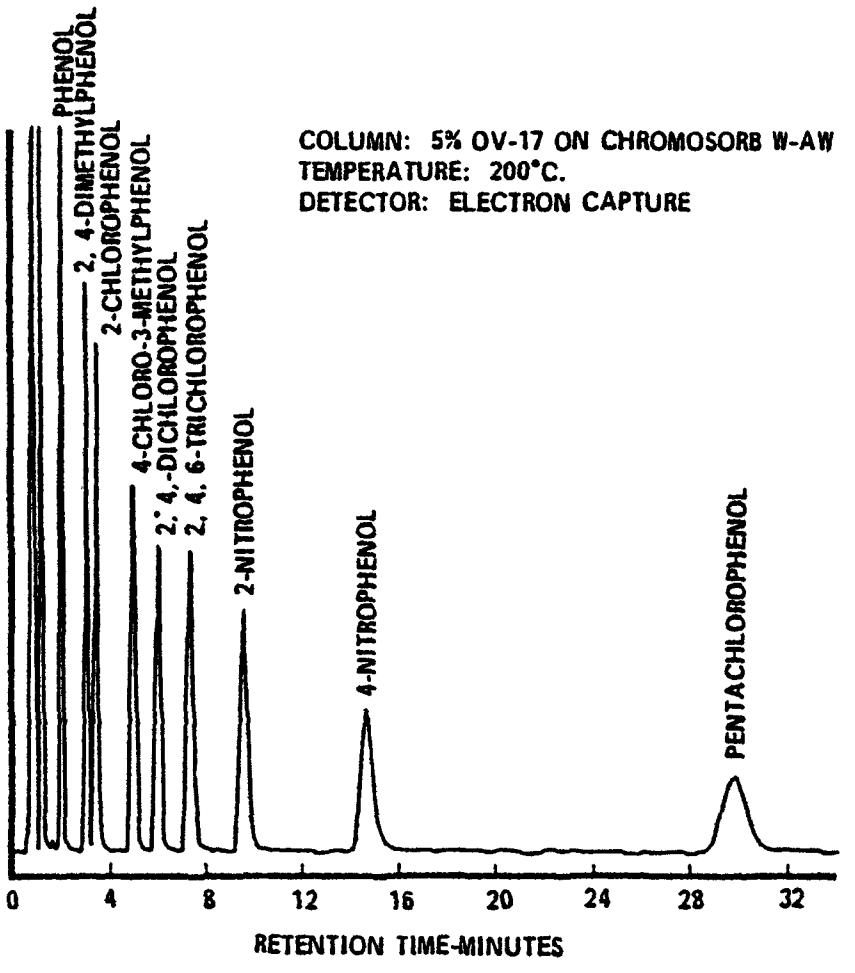

Figure 2. Gas chromatogram of PFB derivatives of phenols

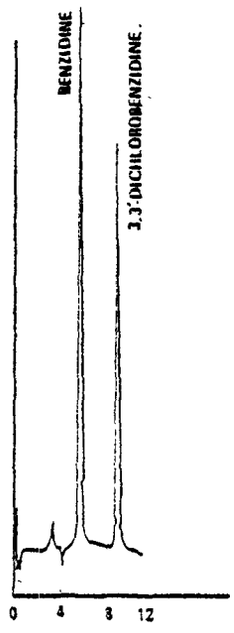

Figure 1. Liquid chromatogram of benzidines

Phthalate Esters—Method 606

1. *Scope and Application.*

1.1 This method covers the determination of certain phthalate esters. The following parameters may be determined by this method:

Parameter:	Storet No.
Benzyl butyl phthalate	34292
Bis(2-ethylhexyl) phthalate	39100
Di-n-butyl phthalate	34110
Di-n-octyl phthalate	34596
Diethyl phthalate	34336
Dimethyl phthalate	34341

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the sample will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of the analysis. Of particular importance is the avoidance of plastics because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K–D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K–570050–1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 . Evaporative flask—500 ml (Kontes K–57001–0500 or equivalent). Attach to concentrator tube with springs. (Kontes K–662750–0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000–0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K–569001–0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture or flame ionization detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—300 mm long × 10 mm ID with coarse fritted disc at bottom and Teflon stopcock (Kontes K–420540–0213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Diethyl Ether—Nanograde, redistilled in glass if necessary.

5.5.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.5.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.6 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in dark in glass container with ground glass stoppers or foil-lined screw caps.

5.7 Alumina—Activity Super I, Neutral, W200 series, (ICN Life Sciences Group, No. 404583).

5.8 Hexane—Pesticide quality.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitudes that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/1 in the final extract, for example, prepare standards at 10 μg/1, 50 μg/1, 100 μg/1, 500 μg/1, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the ph of the sample pH with wide-range paper and adjust to within the range of 5–9 with sodium hydroide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with

20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertial position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 Increase the temperature of the hot water bath to about 80°C. Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and reattach the Snyder column. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. Elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. A 5–ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Cleanup and Separaton.*

10.1 If the entire extract is to be cleaned up by one of the following two procedures, it must be concentrated to about 2 ml. To the concentrator tube in 9.6, add a clean boiling chip and attach a two-ball micro-Snyder column. Prewet the column by adding about 0.5 ml hexane through the top. Place the K–D apparatus on a hot water bath (80°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches about 0.5 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with 0.2 ml of hexane. Proceed with one of the following cleanup procedures.

10.2 Florisil Column Cleanup for Phthalate Esters

10.2.1 Place 100 g of Florisil into a 500 ml beaker and heat for approximately 16 hours at 400°C. After heating transfer to a 500 ml reagent bottle. Tightly seal and cool to room temperature. When cool add 3 ml of distilled water which is free of phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.2.2 Place 10g of this Florisil preparation into a 10 mm ID chromatography column and tap the column to settle the Florisil. Add 1 cm of anhydrous sodium sulfate to the top of the Florisil.

10.2.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane complete the transfer.

10.2.4 Just prior to exposure of the sodium sulfate layer to the air add 40 ml hexane and continue the elution of the column. Discard this hexane eluate.

10.2.5 Next elute the phthalate esters with 100 ml of 20 percent ethyl ether/80 percent hexane (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K–D technique. No solvent exchange is necessary. After concentration and cooling, adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and analyze by gas chromatography.

10.3 Alumina Column Cleanup for Phthalate Esters

10.3.1 Place 100 g of alumina into a 500 ml beaker and heat for approximately 16 hours at 400° C. After heating transfer to a 500 ml reagent bottle. Tightly seal and cool to room temperature. When cool add 3 ml of distilled water which is free from phthalates and interferences. Mix thoroughly by shaking or rolling for 10 minutes and let it stand for at least 2 hours. Keep the bottle sealed tightly.

10.3.2 Place 10 g of this alumina preparation into a 10 mm ID chromatography column and tap the column to settle the alumina. Add 1 cm of anhydrous sodium sulfate to the top of the alumina.

10.3.3 Preelute the column with 40 ml of hexane. Discard this eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 ml sample extract onto the column, using an additional 2 ml of hexane to complete the transfer.

10.3.4 Just prior to exposure of the sodium sulfate layer to the air add 35 ml hexane and continue to elution of the column. Discard this hexane eluate.

10.3.5 Next elute the column with 140 ml of 20 percent ethyl ether/80 percent hexane (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Elute the column at a rate of about 2 ml per minute for all fractions. Concentrate the collected fraction by standard K–D technique. No solvent exchange is necessary. After concentration and cooling adjust the volume of the cleaned up extract to 10 ml in the concentrator tube and analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(B_v)}{(V_i)(V_j)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_1 = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volumeof water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting a interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1- Phthalates." Report for EPA Contract 68-03-2606 (In preparation).

Table I—*Gas Chromatography of Phthalate Esters*

Compound	Retention time (min.)		Detection (μg/l)	
	Col. 1	Col. 2	EC [3]	FID
Dimethyl phthalate	2.03	0.95	0.11	19
Diethyl phthalate	2.62	1.27	0.13	31
Di-n-butyl phthalate	8.65	3.50	0.02	14
Benzyl butyl phthalate	*6.94	**5.11	0.02	15
Bis(2-ethylhexyl) phthalate	*8.92	**10.5	0.04	20
Di-n-octyl phthalate	*16.2	1**8.0	0.11	31

* Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180 cm long × 4 mm ID glass column with carrier gas at 60 ml/min flow rate. Column temperature is 180°C except where * indicates 220°C. Under these conditions R.T. of Aldrin is 5.49 min. at 180°C and 1.84 min at 220°C.

** Supelcoport 100/120 mesh with 3% OV-1 in a 180 cm long × 4 mm ID glass column with carrier gas at 60 ml/mq flow rate. Column temperature is 200°C except where ** indicates 220°C. Under these conditions R.T. of Aldrin is 3.18 min. at 200°C and 1.48 min. at 220°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

BILLING CODE 6560-01-M

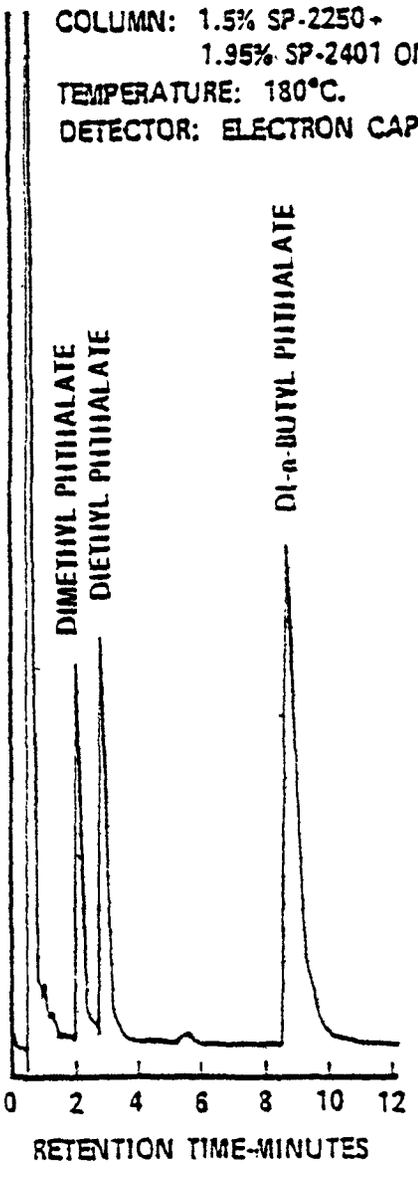

Figure 1. Gas chromatogram of phthalates

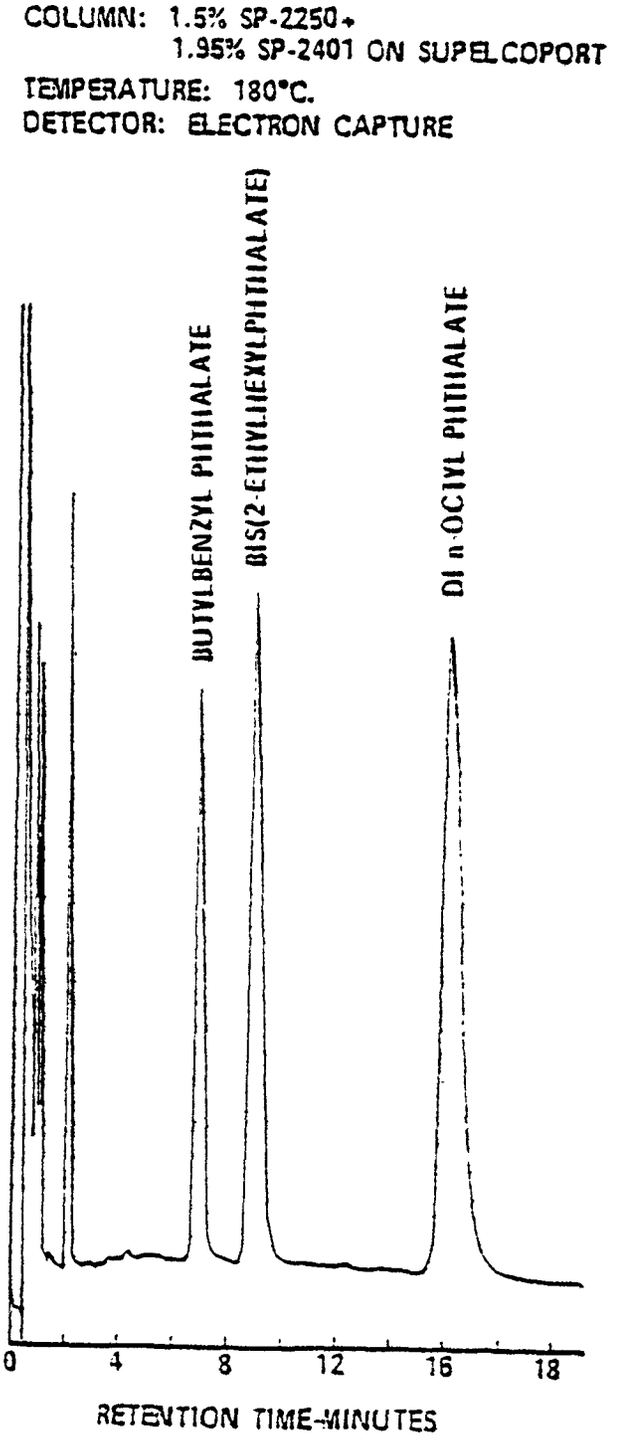

Figure 2. Gas chromatogram of phthalates

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Organochlorine Pesticides and PC3's—Method 608

1. *Scope and Application.*

1.1 This method covers the determination of certain organochlorine pesticides and polychlorinated biphenyls (PCBs). The following parameters may be determined by this method:

Parameter:	Storet No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39259
g-BHC	39340
Chlordane	39350
4,4'-DDD	39310
4,4'-DDE	39320
4,4'-DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39506

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides selected general purpose cleanup procedures to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general cleanup techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 Glassware must be scrupulously clean. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This should be followed by detergent washing in hot water. Rinse with tap water, distilled water, acetone and finally pesticide quality hexane. Heavily contaminated glassware may require treatment in a muffle furnace at 400°C for 15 to 30 minutes. Some high boiling materials, such as PCBs, may not be eliminated by this treatment. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed/stored in a clean environment immediately after drying or cooling to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.4 Interferences by phthalate esters can pose a major problem in pesticide analysis. These materials elute in the 15% and 50% fractions of the Florisil cleanup. They usually can be minimized by avoiding contact with any plastic materials. The contamination from phthalate esters can be completely eliminated with the use of a microcoulometric or electrolytic conductivity detector.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at 1.0 and 10.0 ml level. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Boiling chips—extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required acessories including electron capture or halogen-specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic column—Pyrex, 400 mm × 25 mm OD, with coarse fritted plate and Teflon stopcock (Kontes K-42054-213 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Boiling chips—Hengar granules (Hengar Co.; Fisher Co.) or equivalent.

5.6 Mercury—triple distilled.

5.7 Aluminum oxide—basic or neutral, active.

5.8 Hexane—pesticide residue analysis grade.

5.9 Isooctane (2,2,4-trimethyl pentane)—pesticide residue analysis grade.

5.10 Acetone—pesticide residue analysis grade.

5.11 Diethyl ether—Nanograde, redistilled in glass if necessary.

5.11.1 Must be free of peroxides as indicated by EM Quant test strips (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y., 10523).

5.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

5.12 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use activate each batch at least 16 hours at 130°C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc., so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this factor into 110 and multiplying by 20 grams.

6.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must enploy mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250–ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

9.6 Increase the temperature of the hot water bath to about 80°C. Momentarily remove the Snyder column, add 50 ml of hexane and a new boiling chip and reattach the Snyder column. Pour about 1 ml of hexane into the top of the Snyder column and concentrate the solvent extract as before. The elapsed time of concentration should be 5 to 10 minutes. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and

its lower joint into the concentrator tube with 1–2 ml of hexane, and adjust the volume to 10 ml. A 5-ml syringe is recommended for this operation. stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the sample extract requires no further cleanup, proceed with gas chromatographic analysis. If the sample requires cleanup, proceed to Section 10.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Cleanup and Separation.*

10.1 Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise disfigure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

10.2 Florisil Column Cleanup

10.2.1 Add a weight of Florisil, (nominally 21g,) predetermined by calibration (6.3, 6.4), to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1–2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.

10.2.2 Adjust the sample extract volume to 10 ml and transfer it from the K–D concentrator tube to the Florisil column. Rinse the tube twice with 1–2 ml hexane, adding each rinse to the column.

10.2.3 Place a 500 ml K–D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K–D flask and set aside for later concentration. Elute the column again, using 200 ml of 15% ethyl ether in nexane (Fraction 2), into a second K–D flask. Perform the third elution using 200 ml of 50% ethyl in hexane (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table II.

10.2.4 Concentrate the eluates by standard K–D techniques (9.5), substituting hexane for the glassware rinses and using the water bath at about 85° C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.

10.3 Elemental sulfur will usually elute entirely in Fraction 1. To remove sulfur interference from this fraction or the original extract, pipet 1.00 ml of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1–3 drops of mercury and seal. Agitate the contents of the vial for 15–30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker and shake for 2 hours. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 through 10. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

13.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 10–Pesticides and PCB's." Report for EPA Contract 68–03–2606.

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I. —*Gas Chromatography of Pesticides and PCB's*

Parameter	Retention time (min) Col. 1 [1]	Col.2 [2]	Detection limit (μg/1) [3]
Aldrin	2.40	4.10	0.003
a-BHC	1.35	1.82	0.002
b-BHC	1.90	1.97	0.004
d-BHC	2.15	2.20	0.004
g-BHC	1.70	2.13	0.002
Chlordane	(4)	(4)	0.04
4,4†-DDD	7.83	9.08	0.012
4,4†-DDE	5.13	7.15	0.006
4,4†-DDT	9.40	11.75	0.016
Dieldrin	5.45	7.23	0.006
Endosulfan I	4.50	6.20	0.005
Endosulfan II	8.00	8.28	0.01
Endosulfan sulfate	14.22	10.70	0.03
Endrin	6.55	8.10	0.009
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.002
Heptachlor epoxide	3.50	5.00	0.004
Toxaphene	(4)	(4)	0.40
PCB–1016	(4)	(4)	0.04
PCB–1221	(4)	(4)	0.10
PCB–1232	(4)	(4)	0.10
PCB–1242	(4)	(4)	0.05
PCB–1248	(4)	(4)	0.08
PCB–1254	(4)	(4)	0.08
PCB–1260	(4)	(4)	0.15

[1] Supelcoport 100/120 mesh coated with 1.5% SP–2250/1.95% SP–2401 packed in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[2] Supelcoport 100/120 mesh coated with 3% OV–1 in a 180 cm long x 4 mm ID glass column with 5% Methane/95% Argon carrier gas at 60 ml/min flow rate. Column temperature is 200°C.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

[4] Multiple peak response. See Figures 2–10.

Table II. —*Distribution and Recovery of Chlorinated Pesticides and PCBs Using Florisil Column Chromatography*

Parameter	Recovery (percent) by fraction [1]		
	1(6 pct.)	2 (15 pct.)	3 (50 pct.)
Aldrin	100	.....	.....
a-BHC	100	.....	.....
b-BHC	97	.....	.....
d-BHC	98	.....	.....
g-BHC	100	.....	.....
Chlordane	100	.....	.....
4,4'-DDD	99	.....	.....
4,4'-DDE	96	.....	.....
4o4'-DDT	100	.....	.....
Dieldrin	0	100	.....
Endosulfan I	37	64	.....
Endosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	.....
Endrin aldehyde	0	68	26
Heptachlor	100	.....	.....
Heptachlor epoxide	100	.....	.....
Toxaphene	96	.....	.....
PCB-1016	97	.....	.....
PCB-1221	97	.....	.....
PCB-1232	96	4	.....
PCB-1242	97	.....	.....
PCB-1248	103	.....	.....
PCB-1254	90	.....	.....
PCB-1260	96	.....	.....

[1] From: "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10-Pesticides and PCB's. Report for EPA Contract 68-03-2606."

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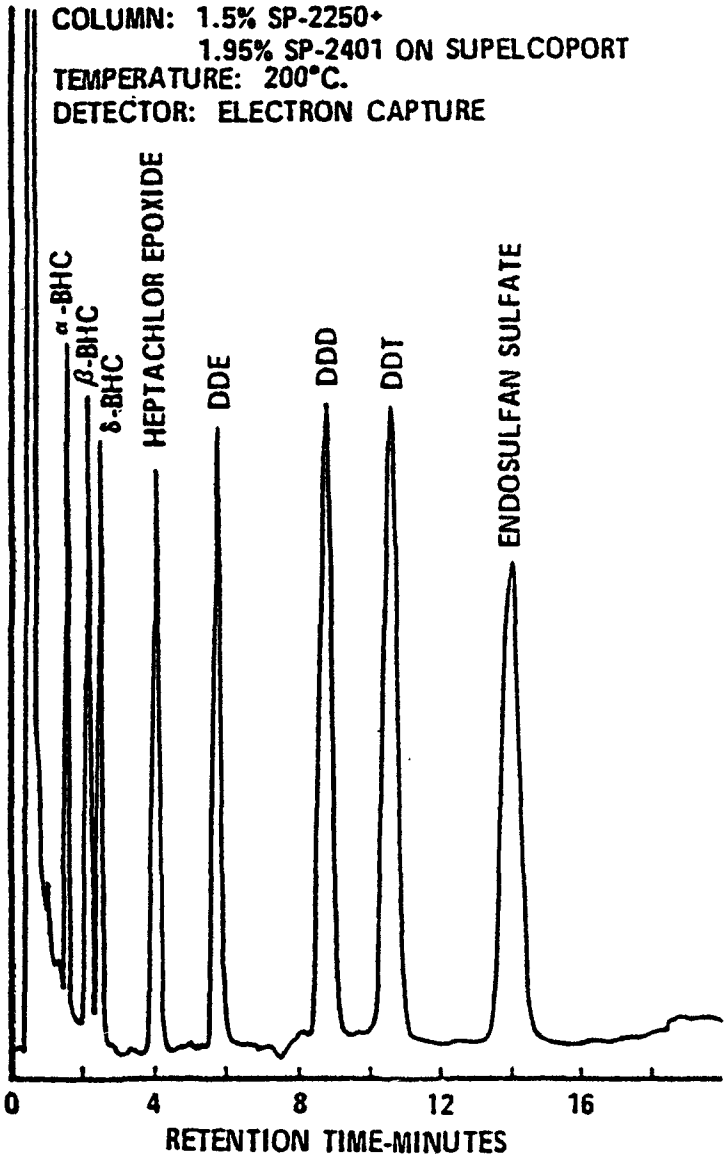

Figure 1. Gas chromatogram of pesticides

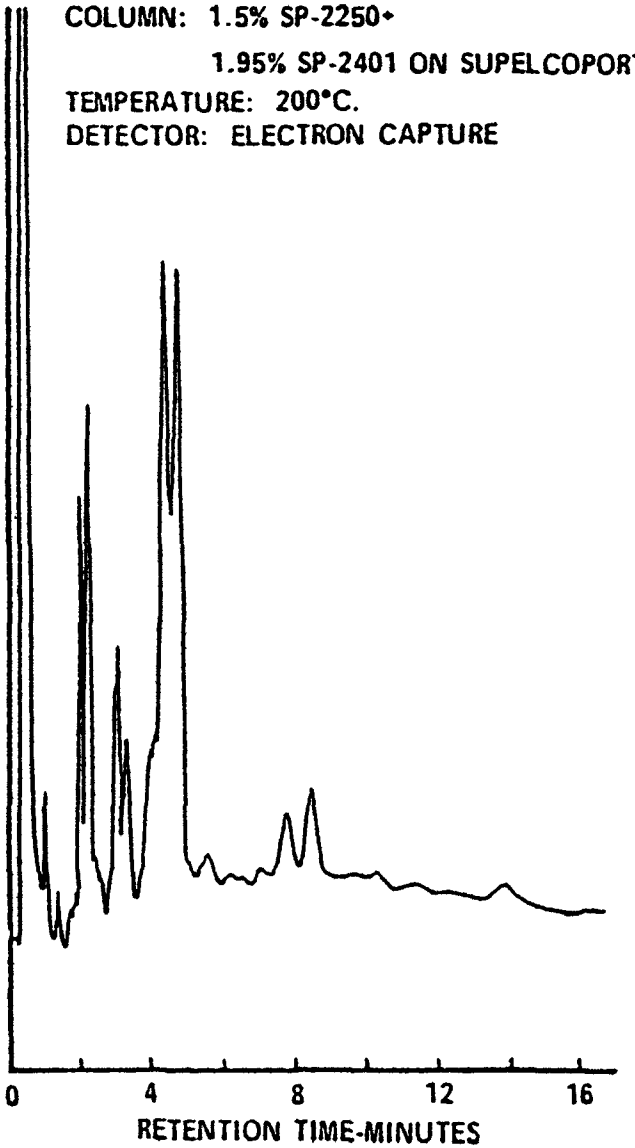

Figure 2. Gas chromatogram of chlordane

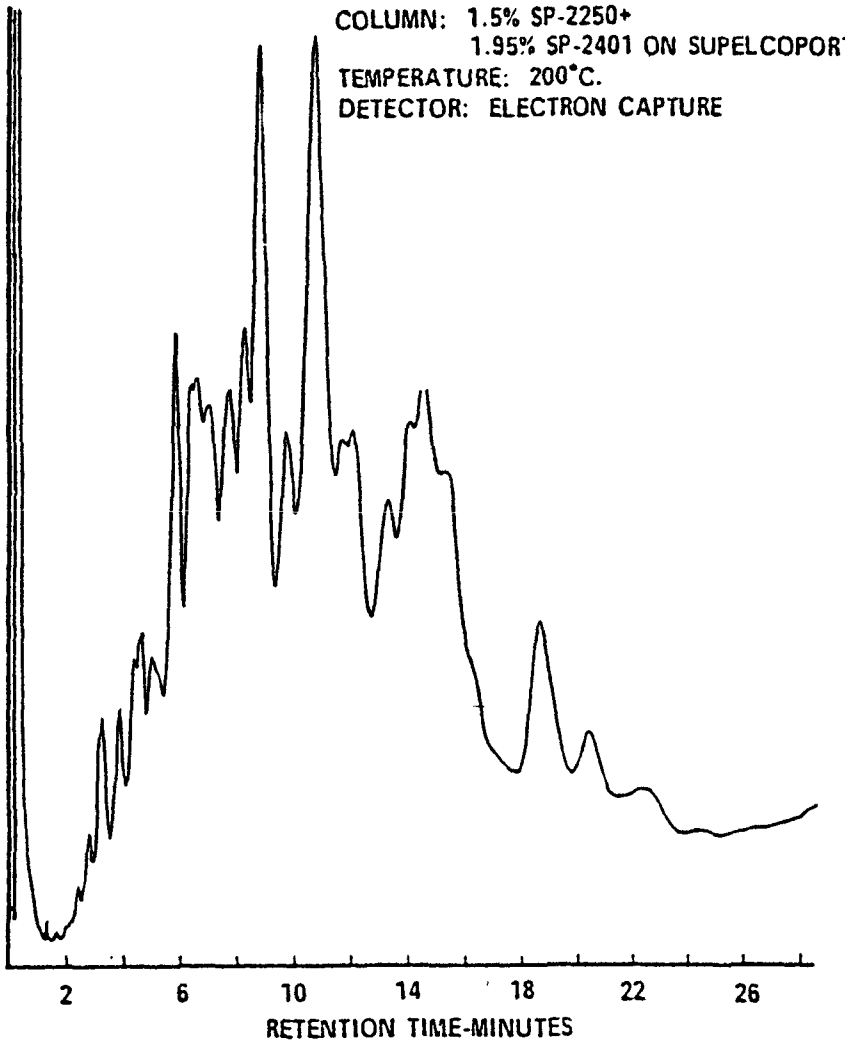

Figure 3. Gas chromatogram of toxaphene

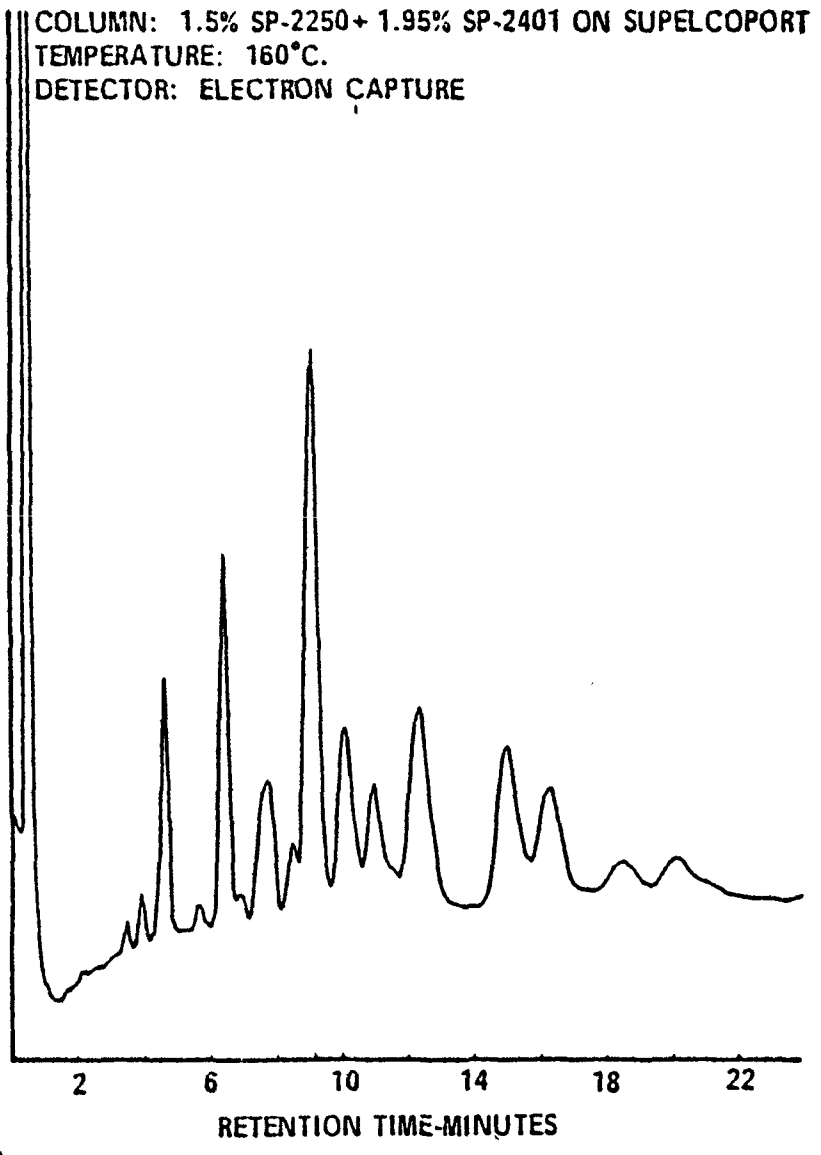

Figure 4. Gas chromatogram of PCB-1016

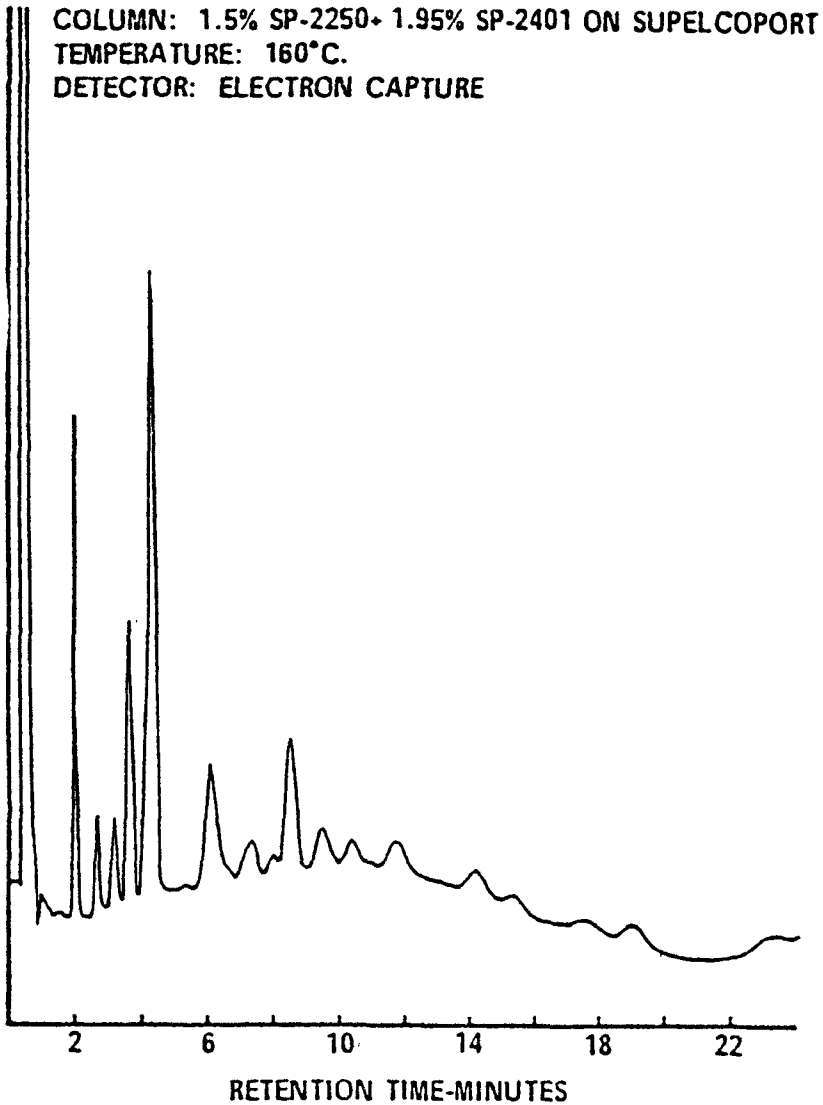

Figure 5. Gas chromatogram of PCB-1221

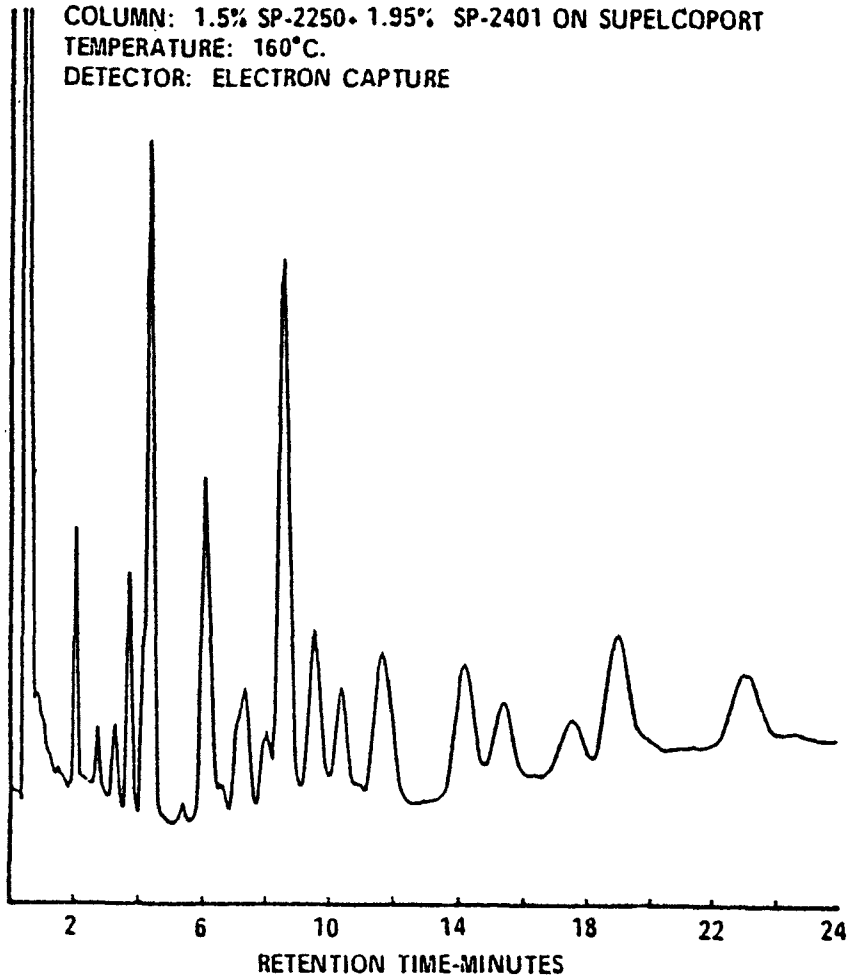

Figure 6. Gas chromatogram of PCB-1232

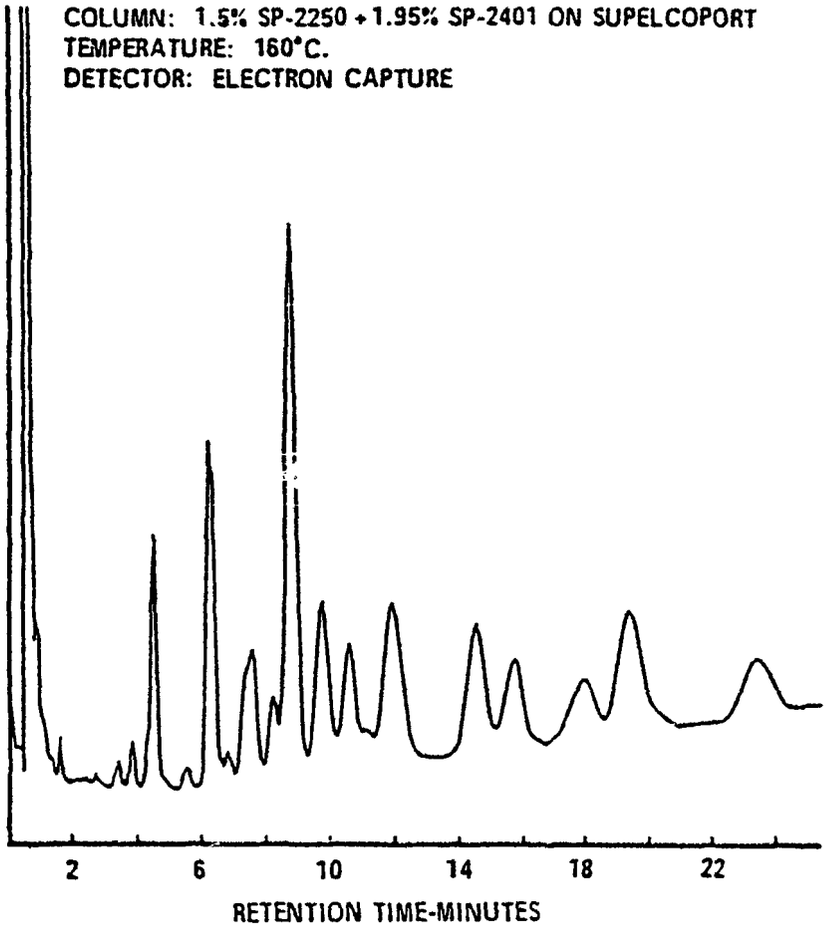

Figure 7. Gas chromatogram of PCB-1242

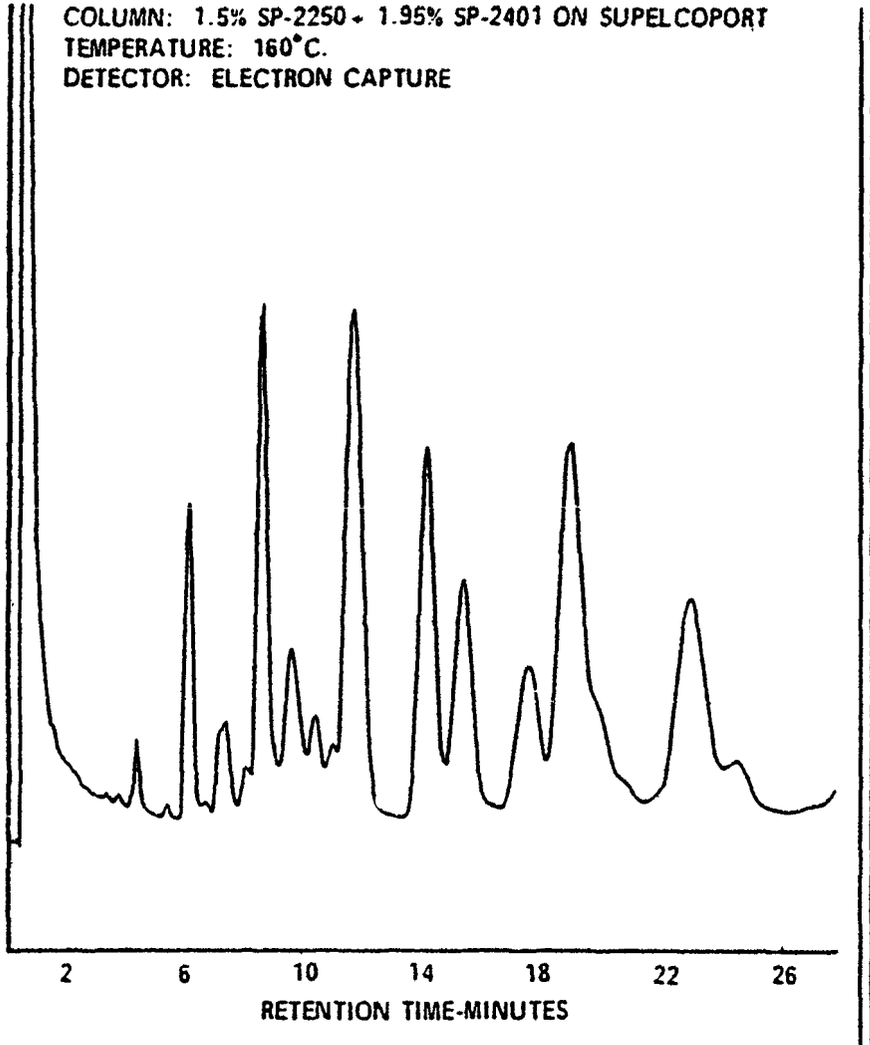

Figure 8. Gas chromatogram of PCB-1248

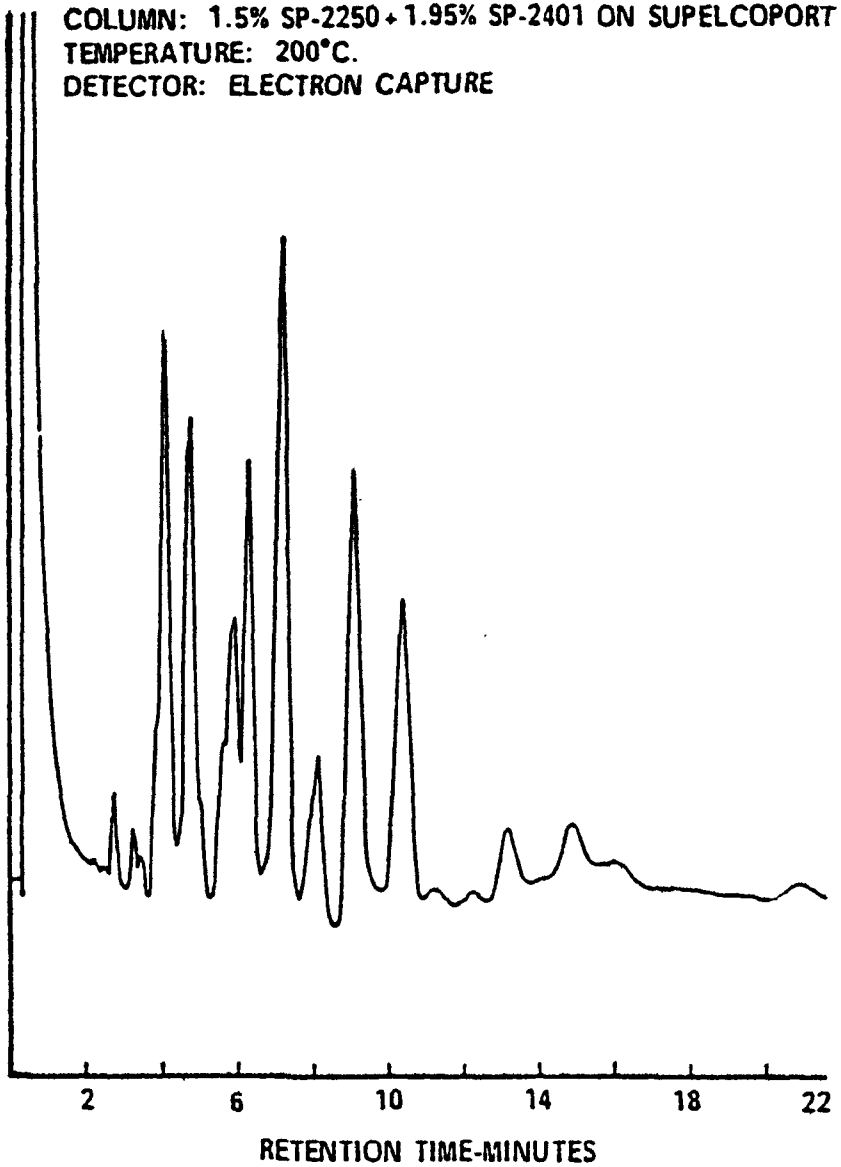

Figure 9. Gas chromatogram of PCB-1254

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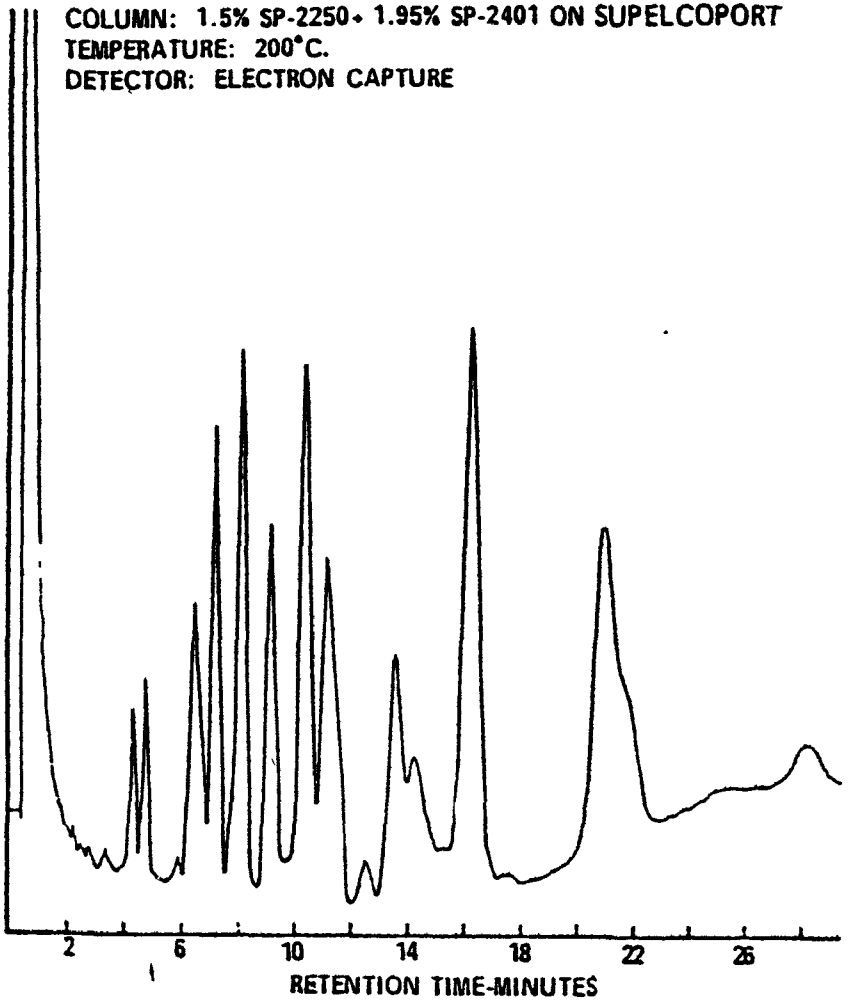

Figure 10. Gas chromatogram of PCB-1260

Nitroaromatics and Isophorone—Method 609

1. *Scope and Application.*

1.1 This method covers the determination of certain nitroaromatics and isophorone. The following parameters may be determined by this method:

Parameter:	Storet No.
Isophorone	34408
Nitrobenzene	34447
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharege Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compunds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and exchanged to toluene while being concentrated to 1.0 ml. Isophorone and nitrobenzene are measured by flame ionization gas chromatography. The dinitrotoluenes are measured by electron capture GC.

2.2 If interferences are encountered, the method provides a general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 *Boiling chips-solvent extracted,* approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including both electron capture and flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—400 mm long x 10 mm ID, with coarse fritted plate on bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water

5.2 Methylene chloride—Pesticide quality or equivalent.

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

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetone, Haxane, Methanol, Toluene—pesticide quality or equivalent.

5.6 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 200°C in glass containers loosely covered with foil.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/1 in the final extract, for example, prepare standards at 10 μg/1, 50 μg/1, 100 μg/1, 500 μg/1, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method

blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techiques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

9.6 Add 1.0 ml toluene to the concentrator tube, and a clean boiling chip. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 ml of methylene chloride to the top. Place this micro-K–D apparatus on a water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of toluene. Adjust the final volume to 1.0 ml and stopper the concentrator tube. and store refrigerated if further processing will not be performed immediately. Unless the sample is known to require cleanup, proceed with gas chromatographic analysis.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Cleanup and Separation.*

10.1 Prepare a slurry of 10g of activated Florisil in 10% methylene chloride in hexane (V/V). Use it to pack a 10 mm ID chromatography column, gently tapping the column to settle the Florisil. Add 1 cm anhydrous sodium sulfate to the top of the Florisil.

10.1.1 Just prior to exposure of the sodium sulfate layer to the air transfer the 1 ml sample extract onto the column using an additional 2 ml of toluene to complete the transfer.

10.1.2 Just prior to exposure of the sodium sulfate layer to the air, add 30 ml 10% methylene chloride in hexane and continue the elution of the column. Elution of the column should be at a rate of about 2 ml per minute. Discard the eluate from this fraction.

10.1.3 Next elute the column with 30 ml of 10% acetone/90% methylene chloride (V/V) into a 500 ml K–D flask equipped with a 10 ml concentrator tube. Concentrate the collected fraction by the K–D technique prescribed in 9.5 and 9.6, including the solvent exchange to 1 ml toluene. This fraction should contain the nitroaromatics and isophorone.

10.1.4 Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Isophorone and nitrobenzene are analyzed by injection of a portion of the extract into a gas chromatograph with a flame ionization detector. The dinitrotoluenes are analyzed by a separate injection into an electron capture gas chromatograph. Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instruments. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by the primary column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units.

V_i = Volume of extract injected (μl).

V_t = Volume of total extract (μl).

V_s = Volume of water extracted (ml).

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.*

The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4-Nitroaromatics and Isophorone," Report for EPA Contract No. 68-03-2624 (In preparation).

Table I. —*Gas Chromatography of Nitroaromatics and Isophorone*

Compound	Retention time (min.)		Detection limit (μg/l)[3]	
	Col. 1[1]	Col. 2[2]	EC	FID
Isophorone	4.49	5.72	.....	5
Nitrobenzene	3.31	4.31	.....	5
2,4-Dinitrotoluene	5.35	6.54	0.06	.....
2,6-Dinitrotoluene	3.52	4.75	0.06	.....

[1] Gas-Chrom Q 80/100 mesh coated with 1.95% OF-1/1.5% OV-17 packed in a 4' × ⅛" OD glass column. FID analyses for IP and NB requires nitrogen carer gas at 44 ml/min and 85°C column temperature. EC analysis for the DNTs requires 10% Methane/90% Argon carrier gas at 44 ml/mn flow rate and 145°C column temperature.

[2] Gas-Chrom Q 80/100 mesh coated with 3% OV-101 packed in a 10' × ⅛" OD glass column. FID analysis of IP and NB requires nitrogen carrier gas at 44 ml/mn flow rate and 100°C column temperature. EC analysis for the DNTs requires 10% Methane/90% Argon carrier gas at 44 ml/mn flow rate and 150°C column temperature.

[3] Detection limit is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

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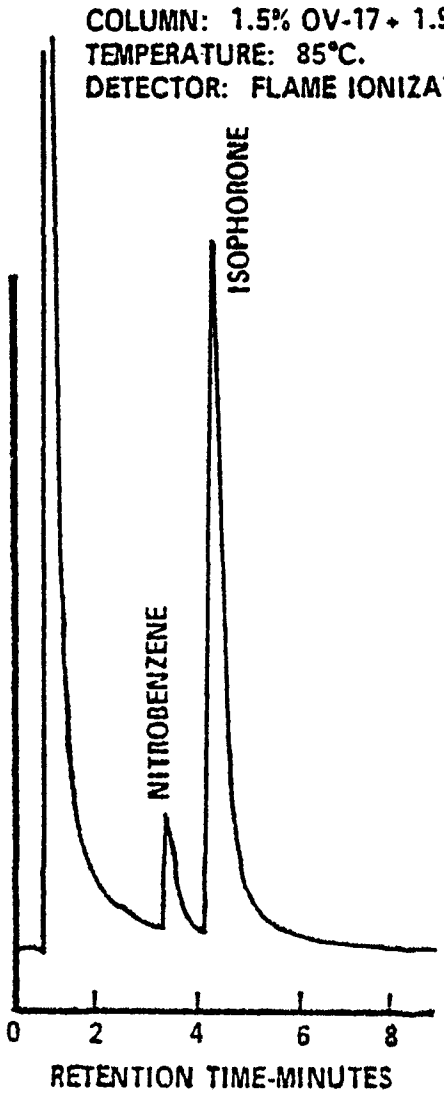

Figure 1. Gas chromatogram of nitrobenzene and isophorone

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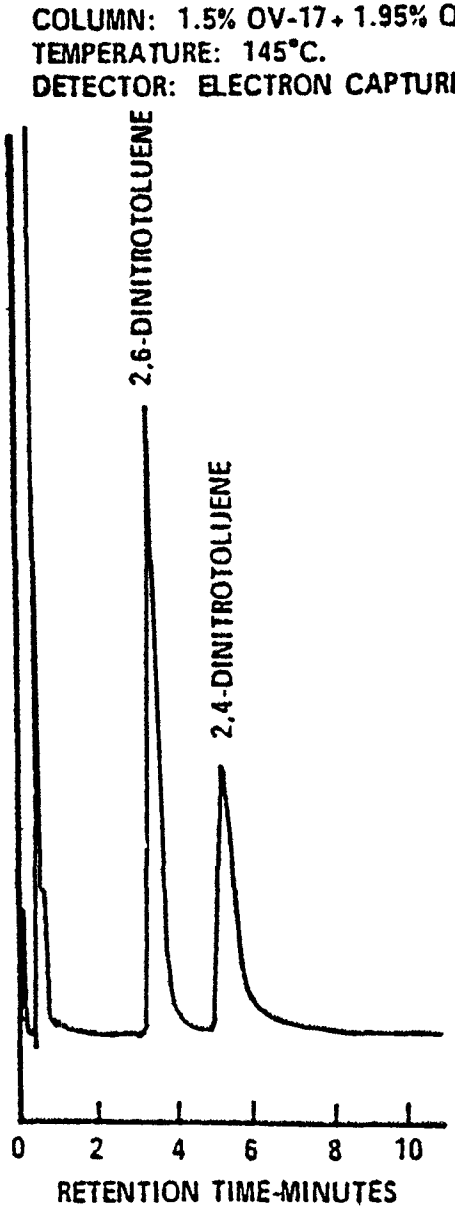

Figure 2. Gas chromatogram of dinitrotoluenes

Polynuclear Aromatic Hydrocarbons—Method 610

1. *Scope and Application.*

1.1 This method covers the determination of certain polynuclear aromatic hydrocarbons (PAH). The following parameters may be determined by this method:

Parameter:	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(a)pyrene	34247
Benzo(b)fluoranthene	34230
Benzo(ghi)perylene	34521
Benzo(k)fluoranthene	34242
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Fluoranthene	34376
Fluorene	34381
Indeno(1,2,3-cd)pyrene	34403
Naphthalene	34696
Phenanthrene	34461
Pyrene	34469

1.2 This method is applicable to the determination of these compounds in muncipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 This method contains both liquid and gas chromatographic approaches, depending upon the needs of the analyst. The gas chromatographic procedure cannot adequately resolve the following four pairs of compounds: Anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b) fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. Unless the purposes of the analysis can be served by reporting a sum for an unresolved pair, the liquid chromatographic approach must be used for these compounds. The liquid chromatographic method will resolve all of the 16 compounds listed above.

1.4 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I for the liquid chromatographic approach represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.5 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract by either High Performance Liquid Chromatography (HPLC) or gas chromatography.

2.2 If interferences are encountered, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of the chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While a general clean-up technique is provided as part of this method, unique samples may require additional clean-up approaches to acheive the sensitivities stated in Table 1.

3.3 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method, other PAH compounds may interfere.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontex K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 HPLC Apparatus:

4.6.1 Gradient pumping system, constant flow.

4.6.2 Reverse phase column, 5 micron HC-ODS Sil-X, 250 mm×2.6 mm ID (Perkin Elmer No. 809-0716 or equivalent).

4.6.3 Fluorescence detector, for excitation at 280 nm and emission at 389 nm.

4.6.4 UV detector, 254 nm, coupled to fluorescence detector.

4.6.5 Strip chart recorder compatible with detectors, (A data system for measuring peak areas is recommended).

4.7 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including dual flame ionization detectors, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.8 Chromatographic column—250 mm long×10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.1.3 Sodium thiosulfate—(ACS) Granular.

5.2 Methylene chloride, Pentane, Cyclohexane, High Purity Water—HPLC quality, distilled in glass.

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

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate

solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Acetonitrile—Spectral quality.

5.6 Silica gel—100/120 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hours at 130° C in a foil covered glass container.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1–5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary HPLC or gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I or II. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

6.3 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt extists over the identification of a peak on the chromatogram, confirmatory techniques such as fraction collection and GC-mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, adjust the sample to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid and add 35 mg sodium thiosulfate per part per million of free chlorine per liter.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a munimum of ten minutes. If the emulsion inteface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10-ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30-ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1-ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparatus volumn of liquid reaches 1-ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2-ml of methylene chloride. A 5-ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.6 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000-ml graduated cylinder. Record the sample volume to the nearest 5-ml.

9.7 If the sample requires cleanup before chromatographic analysis, proceed to Section 10. If the sample does not require cleanup, or if the need for cleanup is unkown, analyze an aliquot of the extract according to Section 11 or Section 12.

10. *Cleanup and Separation.*

10.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add a 1–10-ml aliquot of sample extract (in methylene chloride) and a boiling chip to a clean K–D concentrator tube. Add 4-ml cyclohexane and attach a micro-Snyder column. Prewet the micro-Snyder column by adding 0.5-ml methylene chloride to the top. Place the micro-K–D apparatus on a boiling (100° C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5–10 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5-ml, remove K–D

apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum of cyclohexane. Adjust the extract volume to about 2-ml.

10.2 Silica Gel Column Cleanup for PAHs.

10.2.1 Prepare a slurry of 10g activated silical gel in methylene chloride and place this in a 10 mm ID chromatography column. Gently tap the column to settle the silica gel and elute the methylene chloride. Add 1–2 cm of anhydrous sodium sulfate to the top of the silica gel.

10.2.2 Preelute the column with 40-ml pentane. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2-ml cyclohexane sample extract onto the column, using an additional 2-ml of cyclohexane to complete the transfer.

10.2.3 Just prior to exposure of the sodium sulfate layer to the air, add 25-ml pentane and continue elution of the column. Discard the pentane eluate.

10.2.4 Elute the column with 25-ml of 40% methylene chloride/60% pentane and collect the eluate in a 500-ml K–D flask equipped with a 10-ml concentrator tube. Elution of the column should be at a rate of about 2 ml/min.

10.2.5 Concentrate the collected fraction to less than 10-ml by K–D techniques as in 9.5, using pentane to rinse the walls of the glassware. Proceed with HPLC or gas chromatographic analysis.

11. *High Performance Liquid Chromatography HPLC.*

11.1 To the extract in the concentrator tube, add 4 ml acetonitrile and a new boiling chip, then attach a micro-Snyder column. Increase the temperature of the hot water bath to 95–100° C. Concentrate the solvent as above. After cooling, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 ml acetonitrile. Adjust the extract volume to 1.0 ml.

11.2 Table I summarizes the recommended HPLC column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by this column is shown in Figure 1. Calibrate the system daily with a minimum of three injections of calibration standards.

11.3 Inject 2–5 μl of the sample extract with a high pressure syringe or sample injection loop. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.5 If the peak area measurement is prevented by the pressure of interference, further cleanup is required.

11.6 The UV detector is recommended for the determination of napthalene and acenaphthylene and the fluorescene detector is recommended for the remaining PAHs.

12. *Gas Chromatography.*

12.1 The gas chromatographic procedure will not resolve certain isomeric pairs as indicated in Table II. The liquid chromatographic procedure (Section 11) must be used for these materials.

12.2 To achieve maximum sensitivity with this method, the extract must be concentrated to 1.0 ml. Add a clean boiling chip to the methylene chloride extract in the concentrator tube. Attach a two-ball micro-Snyder column. Prewet the micro-Snyder column by adding about 0.5 ml of methylene chloride to the top. Place this micro-K-D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and water temperature as required to complete the concentration in 5 to 10 minutes. At the proper rate of distillation the balls will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 0.5 ml, remove the K-D apparatus and allow it to drain for at least 10 minutes while cooling. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a small volume of methylene chloride. Adjust the final volume to 1.0 ml and stopper the concentrator tube.

12.3 Table II describes the recommended gas chromatographic column material and operating conditions for the instrument. Included in this table are estimated retention times that should be achieved by this method. Calibrate the gas chromatographic system daily with a minimum of three injections of calibration standards.

12.4 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in ara units.

12.5 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 If the peak ara measurement is prevented by the presence of interferences, further cleanup is required.

13. *Calculations.*

13.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, ug/1} = \frac{(A)\,(B)\,(V_t)}{(V_i)\,(V_w)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (μl)

V_t = Volume of total extract (μl)

V_w = Volume of water extracted (ml)

13.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14. *Accuracy and Precision.*

14.1 The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

"Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 9-PAHs." Report for EPA Contract 68–03–2624 (In preparation).

Table I.—*High Performance Liquid Chromatography of PAH's*

Compound [1]	Retention time (min)	Detection limit (μg/l) [2]	
		UV	Fluorescence
Naphthalene	16.17	2.5	20.0
Acenaphthylene	18.10	5.0	100.0
Acenaphthene	20.14	3.0	4.0
Fluorene	20.89	0.5	2.0
Phenanthrene	22.32	0.25	1.2
Anthracene	23.78	0.10	1.5
Fluoranthene	25.00	0.50	0.05
Pyrene	25.94	0.10	0.05
Benzo(a)anthracene	29.26	0.20	0.04
Chrysene	30.14	0.20	0.5
Benzo(b)fluoranthene	32.44	1.0	0.04
Benzo(k)fluoranthene	33.91	0.30	0.04
Benzo(a)pyrene	34.95	0.25	0.04
Dibenzo(a,h)anthracene	37.06	1.0	0.08
Benzo(ghi)perylene	37.82	0.75	0.2
Indeno(1,2,3-cd)pyrene	39.21	0.30	0.1

[1] HPLC conditions: Reverse phase HC-ODS Sil-X 2.6 × 250 mm Perkin-Elmer column; isocratic elution for 5 min. using 40% acetonitrile/60% water, then linear gradient elution to 100% acetonitrile over 25 minutes; flow rate is 0.5 ml/min.

[2] Detection limit is calculated from the minimum detectable HPLC response being equal to five times the background noise, assuming an equivalent of a 2 ml final volume of the 1 liter sample extract, and assuming an HPLC injection of 2 microliters.

Table II.—*Gas Chromatography of PAHs*

Compound [1]	Retention Time (min)
Naphthalene	4.5
Acenaphthylene	10.4
Acenaphthene	10.8
Fluorene	12.6

Table II.—*Gas Chromatography of PAHs*—Continued

Compound [1]	Retention Time (min)
Phenanthrene	15.9
Anthracene	15.9
Fluoranthene	19.8
Pyrene	20.6
Benzo(a)anthracene	20.8
Chrysene	24.7
Benzo(b)fluoranthene	28.0
Benzo(k)fluoranthene	28.0
Benzo(a)pyrene	29.4
Dibenzo(a,h)anthracene	36.2
Indeno(1,2,3-cd)pyrene	36.2
Benzo(ghi)perylene	38.6

[1]GC conditions: Chromosorb W-AW-DCMs 100/120 mesh coated with 3% OV-17, packed in a 6' x 2 mm ID glass column, with nitrogen carrier gas at 40 ml/min flow rate. Column temperature was held at 100° C for 4 minutes, then programmed at 8°/minute to a final hold at 280° C.

Haloethers—Method 611

1. *Scope and Application*

1.1 This method covers the determination of certain haloethers. The following parameters may be determined by this method:

Parameter:	STORET No.
Bis(2-chloroethyl) ether	34273
Bis(2-chloroethoxy) methane	34278
Bis(2-chloroisopropyl) ether	34283
4-Bromophenyl phenyl ether	34636
4-Chlorophenyl phenyl ether	34641

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of interferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried and concentrated to a volume of 10 ml or less. Chromatographic conditions utilizing a halide specific detector are described which allow for the accurate measurement of the compounds in the extract.

2.2 If interferences are encountered, the method provides a selected general

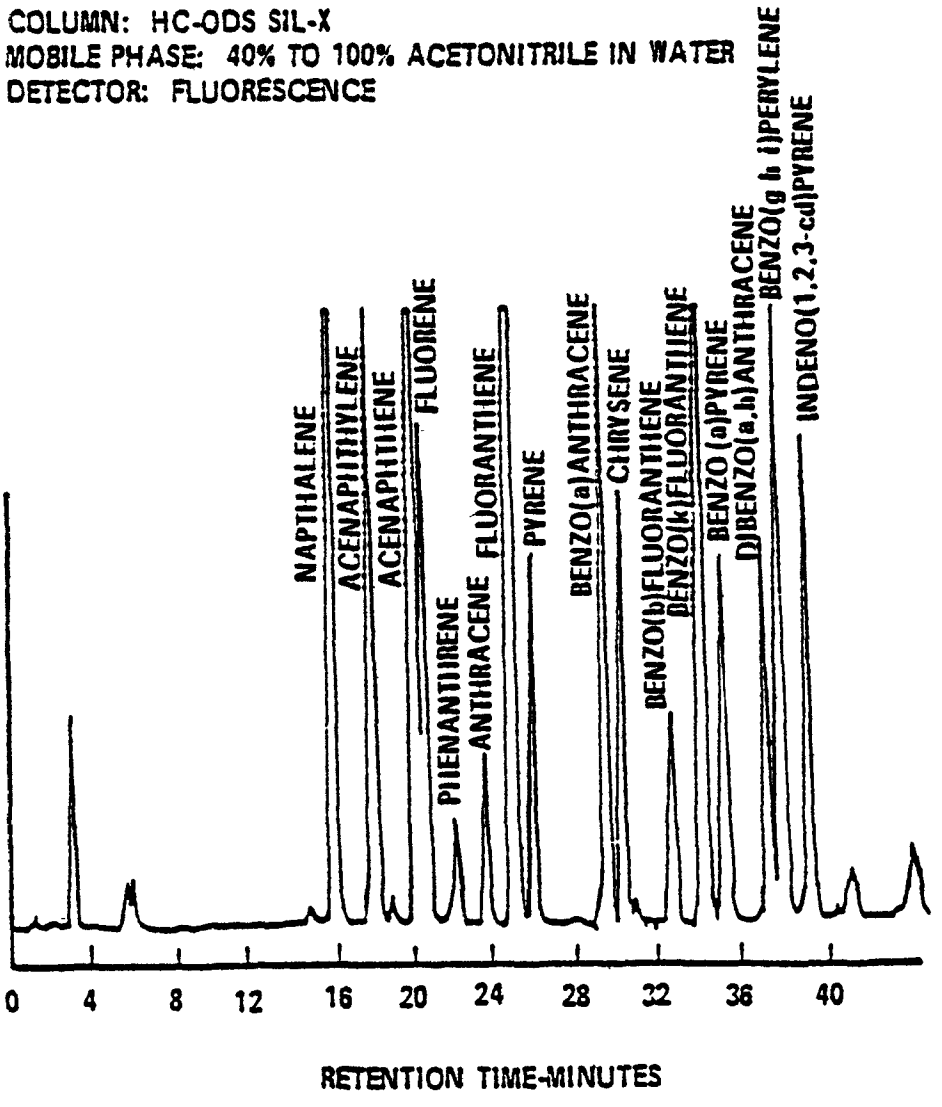

Figure 1. Liquid chromatogram of polynuclear aromatics

purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artificats and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities stated in Table I.

3.3 Dichlorobenzenes are known to coelute with haloethers under some gas chromatographic conditions. If these materials are present together in a sample, it may be necessary to analyze the extract with two different column packings to completely resolve all of the compounds.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample in not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent ecaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 1%0 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including halide specific detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatographic Column—400 mm long x 19 mm ID with coarse fritted plate on bottom and Teflon stopcock (Kontes K-420540-0224 or equivalent).

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid (1+1)—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride—Pesticide quality or equivalent.

5.3 Sodium Sulfate—(ACS) Granular, anhydrous (purified by heating at 400°C for 4 hrs. in a shallow tray).

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 μg/μl by dissolving 0.100 grams of assayed reference material in pesticide quality acetone or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Florisil—PR Grade (60/100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch overnight at 130°C in a foil-covered glass container.

5.6 Hexane, Petroleum ether (boiling range 30-60°C)—pesticide quality or equivalent.

5.7 Diethyl Ether—Nanograde, redistilled in glass, if necessary.

5.7.1 Must be free of peroxides as indicated by EM Quant test strips. (Test strips are available from EM Laboratories, Inc., 500 Executive Blvd., Elmsford, N.Y. 10523.)

5.7.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup 20 ml ethyl alcohol preservative must be added to each liter of ether.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 μg/l in the final extract, for example, prepare standards at 10 μg/l, 50 μg/l, 100 μg/l, 500 μg/l, etc. so that injections of 1-5 μl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 grams.

6.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the

identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K–D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1–2 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

Note.—Haloethers have a sufficiently high volatility that significant losses will occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1–2 ml before removing the K–D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85–90°C. Concentrate the extract as in 9.5 except use hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

9.8 Unless the sample is known to require cleanup, proceed to analysis by gas chromatography.

10. *Cleanup and Separation.*

10.1 Florisil Column Cleanup for Haloethers.

10.1.1 Adjust the sample extract volume to 10 ml.

10.1.2 Place a charge (nominally 20 g but determined in Section 6.3) of activated Florisil in a 19 mm ID chromatography column. After settling the Florisil by tapping column, add about one-half inch layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 50–60 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 300 ml of 6% ethyl ether/94% petroleum ether. Adjust the elution rate to approximately 5 ml/min and collect the eluate in a 500 ml K–D flask equipped with a 10 ml concentrator tube. This fraction should contain all of the haloethers.

10.1.4 Concentrate the fraction by K–D as in 9.5 except prewet the Snyder column with hexane. When the apparatus is cool, remove the column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes some recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by these columns are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 μl of the sample extract using the solvent-flush technique. Smaller (1.0 μl) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 μl, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_t = volume of extract injected (μl)

V_t = volume of total extract (μl)

V_s = volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 2- Haloethers." Report for EPA Contract 68–03–2633 (In preparation).

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, *51*, 29 (1968).

Table I.—*Gas Chromatography of Haloethers*

Compound	Retention time (min.)		Detection limit (ug/L) [3]
	Col. 1 [1]	Col. 2 [2]	
Bis(2-chloroisopropyl) ether	8.41	9.70	0.9
Bis(2-chloroethyl) ether	9.32	9.06	0.5
Bis(2-chloroethoxy) methane	13.1	9.97	0.4
4-Chlorophenyl phenyl ether	19.4	15.0	2.2
4-Bromophenyl phenyl ether	21.2	16.2	1.1

[1] Supelcoport 100/120 mesh coated with 3% SP-1000 packed in 1.8 m long x 2.1 mm ID glass column with ultra-high purity helium carrier/gas at 40 ml/min flow rate. Column temperature is 60°C for 2 minutes after injection then program at 8°C/min to 230°C and hold for 4 minutes. Under these conditions R.T. of Aldrin is 22.6 minutes.

[2] Tenax-GC 60/80 mesh packed in a 1.8 m long x 2.1 mm ID glass column with helium carrier gas at 40 ml/min flow rate. Column temperature 150°C for 4 minutes after injection then program at 16°C/min to 310°C. Under these conditions R.T. of Aldrin is 16.4 minutes.

[3] Detection is calculated from the minimum detectable GC response being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a FC injection of 5 microliters. These values were collected using the Tracor 700 Hall electrolytic conductivity detector with furnace temperature 900°C, transfer line 250°C, 95% ethanol electrolyte at 0.3 ml/min flow rate, and hydrogen reaction gas at 60 ml/min.

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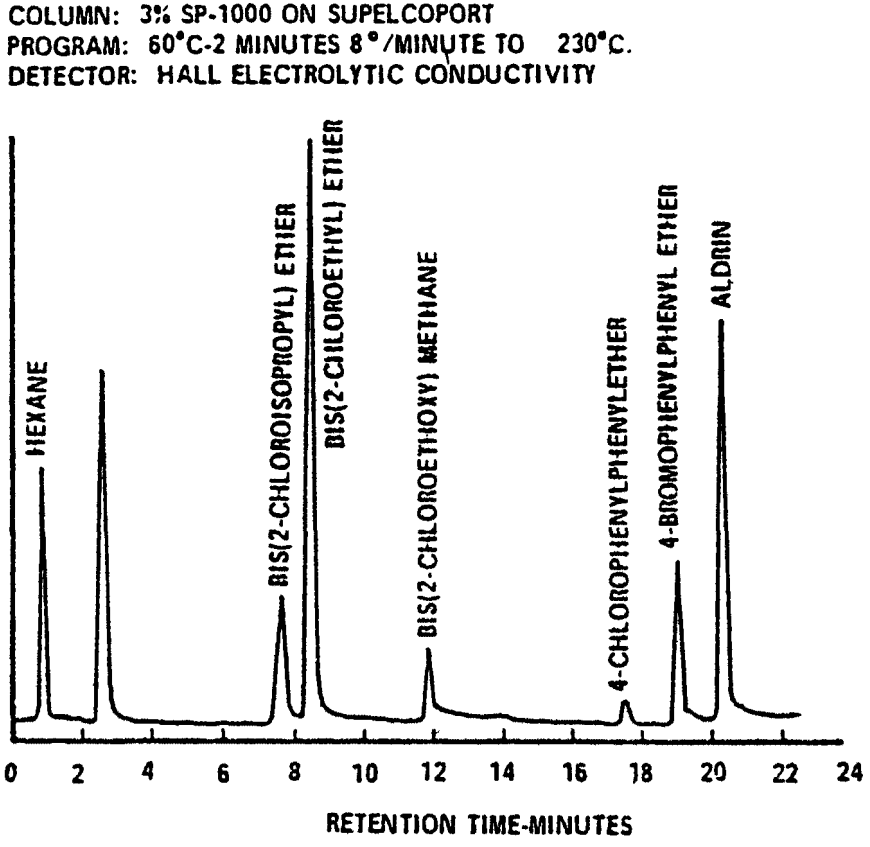

Figure 1. Gas chromatogram of haloethers

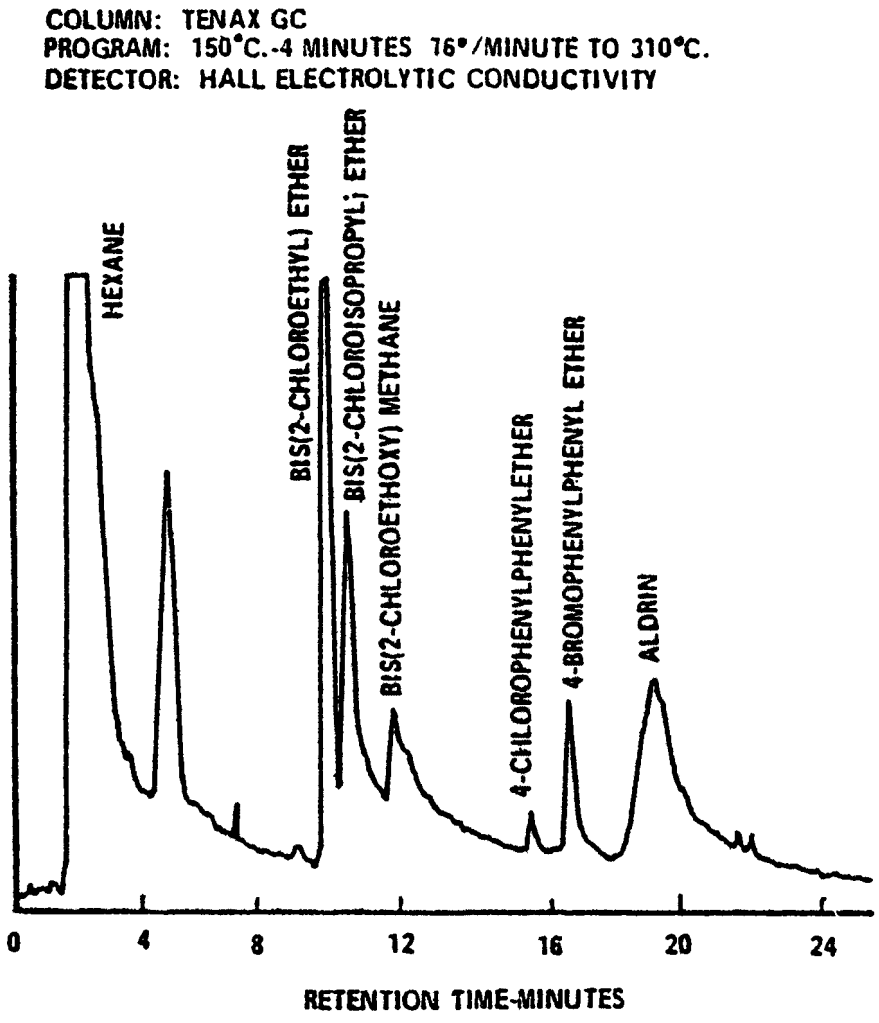

Figure 2. Gas chromatogram of haloethers

Chlorinated Hydrocarbons—Method 612

1. *Scope and Application.*

1.1 This method covers the determination of certain chlorinated hydrocarbons. The following parameters may be determined by this method.

Parameter:	STORET No.
Hexachlorocyclopentadiene	34386
Hexachlorobenzne	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
1,2-Dichlorobenzene	34536
1,2,4-Drichlorobenzene	34551
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
2-chloronaphthalene	34581

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutant Discharge Elimination System (NPDES). As such, it presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds above, he must develop independent protocols for the verification of identity.

1.3 The sensitivity of this method is ususally dependent upon the level of interferences rather than instrumental limitations. The limits of detection listed in Table I represent sensitivities that can be achieved in wastewaters in the absence of inteferences.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1-liter sample of wastewater is extracted with methylene chloride using separatory funnel techniques. The extract is dried by passing through a sodium sulfate column and concentrated to a volume of 10 ml or less. Chromatographic conditions are described which allow for the accurate measurement of the compounds in the extract.

2.2 If inteferences are encountered or expected, the method provides a selected general purpose cleanup procedure to aid the analyst in their elimination.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from inteferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. While general clean-up techniques are provided as part of this method, unique samples may require additional cleanup approaches to achieve the sensitivities states in Table 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to screw on to the sample bottles. Caps must be lined with Teflon. Foil may be substituted if sample is not corrosive and the foil is found to be interference free.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 250 ml. Sample containers must be kept refrigerated during sampling. No tygon or rubber tubing may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock.

4.3 Drying column—20 mm ID pyrex chromatographic column with coarse frit.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0121 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569001-0219 or equivalent).

4.4.5 Boiling chips—solvent extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including electron capture detector, column supplies, recorder, gases, syringes. A data system for measuring peak areas is recommended.

4.7 Chromatography column—300 mm long × 10 mm ID with coarse fritted disc at bottom and Teflon stopcock.

5. *Reagents.*

5.1 Preservatives:

5.1.1 Sodium hydroxide—(ACS) 10 N in distilled water.

5.1.2 Sulfuric acid—(ACS) Mix equal volumes of conc. H_2SO_4 with distilled water.

5.2 Methylene chloride, Hexane and Petroleum ether (boiling range 30–60°C)—Pesticide quality or equivalent.

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

5.4 Stock standards—Prepare stock standard solutions at a concentration of 1.00 µg/ul by dissolving 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and diluting to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

5.5 Florisil—PR grade (60/100 mesh); purchase activated at 1250°F and store in the dark in glass containers with glass stoppers or foil-lined screw caps. Before use, activate each batch at 130°C in foil-covered glass containers.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations covering two or more orders of magnitude that will completely bracket the working range of the chromatographic system. If the sensitivity of the detection system can be calculated from Table I as 100 µg/1 in the final extract, for example, prepare standards at 10 µg/1, 50 µg/1, 100 µg/1, 500 µg/1, etc. so that injections of 1–5 µl of each calibration standard will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Table I. By injecting calibration standards, establish the sensitivity limit of the detector and the linear range of the analytical system for each compound.

6.3 The cleanup procedure in Section 10 utilizes Florisil chromatography. Florisil from different batches or sources may vary in absorption capacity. To standardize the amount of Florisil which is used, the use of lauric acid value (Mills, 1968) is suggested. The referenced procedure determines the

adsorption from hexane solution of lauric acid (mg) per gram Florisil. The amount of Florisil to be used for each column is calculated by dividing this ratio by 110 and multiplying by 20 grams.

6.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interferences from the reagents.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers, leaving a minimum headspace. Conventional sampling practices should be followed, except that the bottle must not be prewashed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, the sample should be adjusted to a pH range of 6.0–8.0 with sodium hydroxide or sulfuric acid.

8.3 All samples should be extracted immediately and must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction.*

9.1 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Check the pH of the sample with wide-range pH paper and adjust to within the range of 5–9 with sodium hydroxide or sulfuric acid.

9.2 Add 60 ml methylene chloride to the sample bottle, seal, and shake 30 seconds to rinse the inner walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.3 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.4 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500-ml Kuderna-Danish (K-D) flask equipped with a 10 ml concentrator tube. Rinse the Erlenmeyer flask and column with 20–30 ml methylene chloride to complete the quantitative transfer.

9.5 Add 1–2 clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride to the top. Place the K–D apparatus on a hot water bath (60–65° C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15–20 minutes. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1–2 ml, remove the K–D apparatus and allow it to drain for at least 10 minutes while cooling.

Note.—The dichlorobenzenes have a sufficiently high volatility that significant losses may occur in concentration steps if care is not exercised. It is important to maintain a constant gentle evaporation rate and not to allow the liquid volume to fall below 1–2 ml before removing the K-D from the hot water bath.

9.6 Momentarily remove the Snyder column, add 50 ml hexane and a new boiling chip and replace the column. Raise the temperature of the water bath to 85–90° C. Concentrate the extract as in 9.5, except using hexane to prewet the column. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml of hexane. A 5-ml syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately.

9.7 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 ml graduated cylinder. Record the sample volume to the nearest 5 ml.

9.8 Unless the sample is known to require cleanup, proceed to analysis by gas chromatography.

10. *Cleanup and Separation.*

10.1 Florisil column cleanup for chlorinated Hydro-carbons.

10.1.1 Adjust the sample extract to 10 ml.

10.1.2 Place a 12 gram charge of activated Florisil (see 6.3) in a 10 mm ID chromatography column. After settling the Florisil by tapping the column, add a 1–2 cm layer of anhydrous granular sodium sulfate to the top.

10.1.3 Pre-elute the column, after cooling, with 100 ml of petroleum ether. Discard the eluate and just prior to exposure of the sulfate layer to air, quantitatively transfer the sample extract into the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 ml petroleum ether and collect the eluate in a 500 ml K–D flask equipped with a 10 ml concentrator tube. This fraction should contain all of the chlorinated hydrocarbons.

10.1.4 Concentrate the fraction by K–D as in 9.5 except prewet the column with hexane. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1–2 ml hexane. Analyze by gas chromatography.

11. *Gas Chromatography.*

11.1 Table I summarizes the recommended gas chromatographic column materials and operating conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. Examples of the separations achieved by this column are shown in Figures 1 and 2. Calibrate the system daily with a minimum of three injections of calibration standards.

11.2 Inject 2–5 ul of the sample extract using the solvent-flush technique. Smaller (1.0 ul) volumes can

be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.

11.3 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

11.4 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

12. *Calculations.*

12.1 Determine the concentration of individual compounds according to the formula:

$$\text{Concentration, } \mu g/l = \frac{(A)(B)(V_t)}{(V_i)(V_s)}$$

Where:

A = Calibration factor for chromatographic system, in nanograms material per area unit.

B = Peak size in injection of sample extract, in area units

V_i = Volume of extract injected (ul)

V_t = Volume of total extract (ul)

V_s = Volume of water extracted (ml)

12.2 Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

13. *Accuracy and Precision.* The U.S. EPA Environmental Monitoring and Support Laboratory in Cincinnati is in the process of conducting an interlaboratory method study to determine the accuracy and precision of this test procedure.

Bibliography

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 3—Chlorinated Hydrocarbons and Category 8—Phenols." Report for EPA Contract 68-03-2625 (In preparation).

2. Mills, P. A., "Variation of Florisil Activity: Simple Method for Measuring Absorbent Capacity and Its Use in Standardizing Florisil Columns." Journal of the Association of Official Analytical Chemists, 51, *29* (1968).

Table I.—*Gas Chromatography of Chlorinated Hydrocarbons*

Compound	Retention time (min.) col. 1 [1]	Detection limit ($\mu g/l$) [2]
1,3-dichlorobenzene	4.0	0.009
1,4-dichlorobenzene	4.3	0.018
Hexachloroethane	4 8	0.001
1,2-dichlorobenzene	5.3	0 012
Hexachlorobutadiene	11 6	0.001
1,2,4-trichlorobenzene	12.4	0.006
Hexachlorocyclopentadiene	*1.5	0.001
2-chloronaphthalene	*2.5	0.015
Hexachlorobenzene	*7 0	0 001

[1] Gas Chrom Q 80/100 mesh coated with 1.5% OV-1/1.5% OV-225 packed in a 1.8 m long x 2 mm ID glass column with 5% Methane/95% Argon carrier gas at 30 ml/min flow rate. Column temperature is 75° C except where * indicates 160° C. Under these conditions R.T. of Aldrin is 18.8 minutes at 160° C.

[2] Detection limit is calculated from the minimum detectable GC response of the electron capture detector being equal to five times the GC background noise, assuming a 10 ml final volume of the 1 liter sample extract, and assuming a GC injection of 5 microliters.

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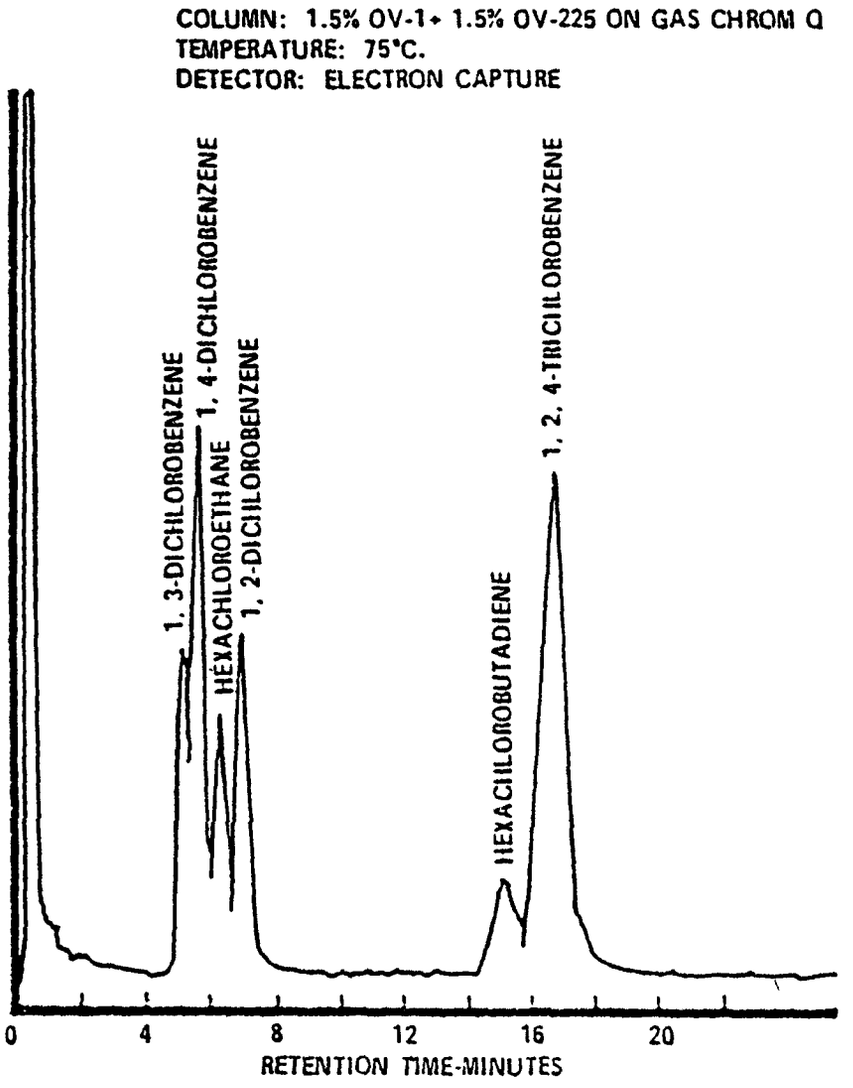

Figure 1. Gas chromatogram of chlorinated hydrocarbons

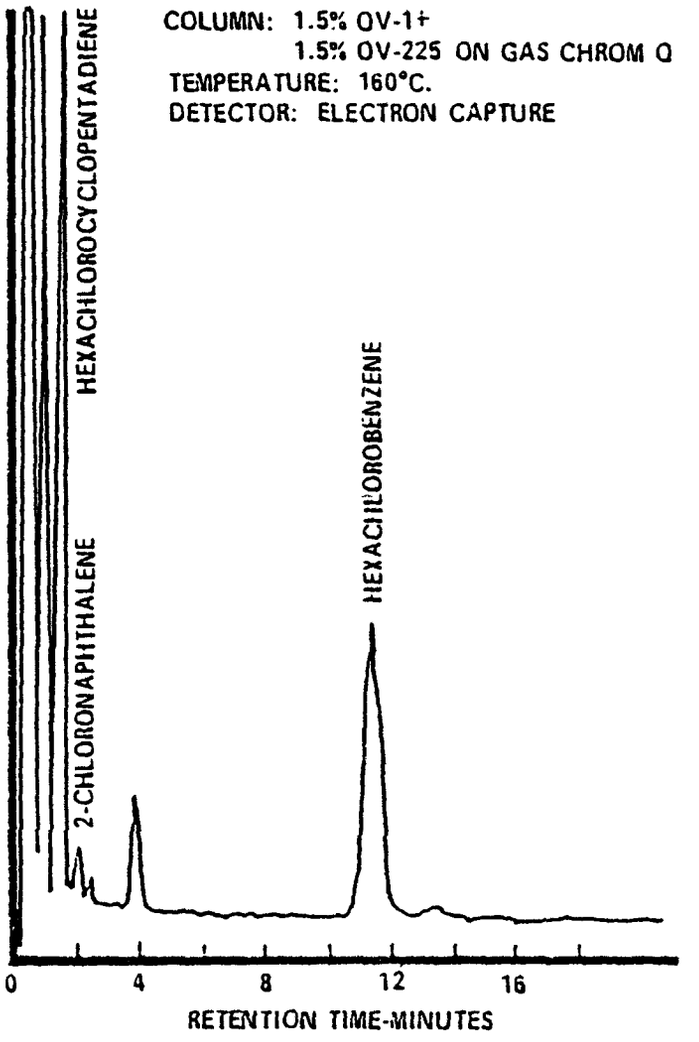

Figure 2. Gas chromatogram of chlorinated hydrocarbons

Purgeables—Method 624

1. *Scope and Application.*

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

21. A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

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

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1. Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ⅛ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60–80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten centimeter traps may be used providing that the recoveries are comparable to the 25 cm traps.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD.x 0.90 to 0.105 in. ID) packed with 1% SP–1000 coated on 60/80 mesh Carbopack B preceded by a 5-cm precolumn packed with 1% SP–1000 coated on 60/80 mesh Chromosorb W. A glass column (¼ in OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in OD x 0.09 to 0.105 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (¼ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–260 in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be

computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 *Trap Materials*

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.3 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methanol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 μl syringe, immediately add 2 to 3 drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a 5-ml valved gas-tight syringe with the reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methyl alcohol menicus. Slowly inject the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle equipped with a Teflon cap liner.

5.5.4 Calculate the concentration in mg per ml (equivalent to μg per μl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 μg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. *Calibration.*

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 μg/l, for example, prepare secondary methanolic standards at 100 μg/l, and 500 μg/l, so that aqueous standards prepared from thee secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the limit of detection requirements in Table 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample analysis may begin.

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in μg.

C_s is the amount of the pollutant standard in μg.

The relative response ratio for each pollutant should be known for at least two concentration values—50 ng injected to approximate 10 μg/l and 500 ng to approximate the 100 μg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. The response factor (RF) must be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note.—EPA, through its contractors and certain of its Regional Laboratories, is currently evaluating selected compounds for

use as internal standards in the analysis of organics by purge and trap.

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. Quality Control.

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.

8. Sample Collection, Preservation, and Handling.

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 μg/40 ml) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. Sample Extraction and Gas Chromatography.

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 μl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ±.05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap, with an inert gas, at 20 to 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. Gas Chromatography—Mass Spectrometry.

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operting conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 5.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS–1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

Sample size—5.0 ml.
Purge gas—Helium, high purity grade.
Purge time—12 minutes.
Purge flow—40 ml/min.
Trap dimensions—⅛ in. O.D. (0.105 in. I.D.)x25 cm long.
Trap sorbent—Tenax-GC, 60/80 mesh (15 cm), plus Type 15 silica gel, 35/60 mesh (8 cm).
Desorption flow—20 ml/min.
Desorption time—4 min.
Desorption temperature—180° C.

10.4 Mass Spectrometer Parameters.

Electron energy—70 volts (nominal).
Mass range—20–27, 33–260 amu.
Scan time—6 seconds or less.

10.5 Calibration of the gas-chromatography-mass spectrometry (GC–MS system—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP or BFB.

10.5.1 To use DFTPP, remove the analytical column and substitute a column more appropriate to the boiling point of the reference compound (e.g. 3% SP–2250 on Supelcoport). Inject a solution containing 50 ng DFTPP and check to insure that the performance criteria listed in Table 3 are met.

10.5.2 To use BFB, inject a solution containing 20 ng BFB and check to insure that the performance criteria listed in Table 4 are met.

10.5.3 If the system performance criteria are not met for either test, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

10.6 Analyze an internal or external calibration standard to develop response factors for each compound.

11. *Qualitative and Quantitative Determination.*

11.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and at least two other ions (if available) listed in Table 5. The criteria below must be met for a qualitative identification.

11.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

11.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

11.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC-MS system or from a reference library.

11.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

11.2 The primary ion listed in Table 5 is to be used to quantify each compound. If the sample produces an interference for the primary ion, use a secondary ion to quantify.

11.3 For low concentrations, or direct aqueous injection of acrylonitrile and acrolein, the characteristic masses listed for the compounds in Table 5 may be used for selected ion monitoring (SIM). SIM is the use of a mass spectrometer as a substance selective detector by measuring the mass spectrometric response at one or several characteristic masses in real time.

11.4 Internal Standard Method Calculations—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of the pollutant (C_o) in μg/l in the sample is calculated using equation 2,

$$\text{Eq. (2)} C_o = \frac{(A_x)(C_{is})}{(A_{is})(RF)(V_o)}$$

Where:

V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.5. To quantify, add the internal standard to the 5.0-ml sample no more than a few minutes before purging to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve.

11.5 Extenral Standard Method Calculations—The concentration of the unknown can be calculated from the slope and intercept of the multiple point calibration curve. The unknown concentration can be determined using equation 3.

$$\text{Eq. (3) micrograms per liter} = \text{ng/ml} = \frac{(A)}{(V_s)}$$

Where:

A = Mass of compound from calibration curve (ng/5 ml).
V_s = volume of water purged (5 ml).

11.6 An alternate external standard approach for purgeables utilizes a single point calibration. Prepare and analyze a reference standard that closely approximates the response for each component in a sample. Calculate the concentration in the sample using Equation 4.

$$\text{Eq. 4 micrograms per liter} = \frac{(A)(B)}{(C)}$$

Where:

A = area of the unknown
B = concentration of standard (μg/l)
C = area of the standard.

11.7 Report all results to two significant figures. When duplicate and spiked samples are analyzed, all data obtained should be reported. Report results in micrograms per liter without correction for recovery data.

12. *References.*

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4. ASTM Annual Standards—Water, part 31, Method D2908 "Standard Recommended Practice for Measuring Water by Aqueous-Injection Gas Chromatography."

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2. "Proceedings: Seminar on Analytical Methods for Priority Pollutants," Volume 1—Denver, Colorado, November 1977; Volume 2—Savannah, Georgia, May 1978; Volume 3—Norfolk, Virginia, March 1979; USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1

Parameter	STORET No.
Acrolein	34210
Acrylonitrile	34215
Benzene	34236
Bromomethane	34413
Bromodichloromethane	32101
Bromoform	32104
Carbon Tetrachloride	32102
Chlorobenzene	34301
Chloroethane	34311
2-Chloroethylvinyl ether	34576
Chloroform	32106
Chloromethane	34418
Dibromochloromethane	34106
1,1-Dichloroethane	34496

Table 1—Continued

Parameter	STORET No.
1,2-Dichloroethane	34531
1,1-Dichloroethene	34501
trans-1,2-Dichloroethene	34546
1,2-Dichloropropane	34541
cis-1,3-Dichloropropene	34561
trans-1,3-Dichloropropene	34561
Ethylbenzene	34371
Methylene chloride	34423
1,1,2,2-Tetrachloroethane	34516
Tetrachloroethene	34475
1,1,1-Trichloroethane	34506
1,1,2-Trichloroethane	34511
Trichloroethene	39180
Trichlorofluoromethane	34488
Toluene	34010
Vinyl chloride	39175

Table 2.—*Gas Chromatography of Organics by Purge and Trap* [1]

Compound	Retention time (minutes) Col. 1 [2]	Col. 2 [3]	Limit of detection [4] (μg/l)
chloromethane	1.50	2.10	10
bromomethane	2.17	2.50	10
vinyl chloride	2.67	2.57	10
chloroethane	3.33	2.82	10
methylene chloride	5.25	4.03	10
trichlorofluoromethane	7.18	5.14	10
1,1-dichloroethene	7.92	5.25	10
bromochloromethane (SS)	8.48	6.31	----
1,1-dichloroethane	9.30	6.48	10
trans-1,2-dichloroethene	10.08	6.81	10
chloroform	10.56	7.70	10
1,2-dichloroethane	11.40	8.29	10
1,1,1-trichloroethane	12.60	9.26	10
carbon tetrachloride	13.02	9.45	10
bromodichloromethane	13.65	10.36	10
1,2-dichloropropane	14.92	11.30	10
trans-1,3-dichloropropene	15.22	11.70	10
trichloroethene	15.60	11.98	10
dibromochloromethane	16.48	12.86	10
1,1,2-trichloroethane	16.52	12.86	10
cis-1,3-dichloropropene	16.53	12.86	10
benzene	----	12.95	10
2-chloroethylvinyl ether	18.00	13.71	10
2-bromo-1-chloropropane (SS)	----	13.82	----
bromoform	19.23	15.41	10
1,1,2,2-tetrachloroethane	21.62	17.70	10
tetrachloroethene	21.67	17.44	10
1,4-dichlorobutane (SS)	----	18.13	----
toluene	----	18.53	10
chlorobenzene	24.18	20.57	10
ethylbenzene	----	25.06	10
acrolein	----	----	[5]100
acrylonitrile	----	----	[5]100

[1] Eight ft. stainless steel column (1/8 in ODx0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Carbopack B preceded by a 1 ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 1% SP-1000 coated on 60/80 mesh Chromosorb W. (A glass column (1/4 in. ODx2 mm ID) may be substituted). Carrier gas helium at 40 ml/min. Temperature program: 3 min isothermal at 45° C, then 8°/min to 220°, hold at 220° for 15 minutes.

[2] Eight ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (1/8 in. ODx0.1 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (1/4 in. ODx2 mm ID) may be substituted. Carrier gas: helium at 40 ml/min. Temperature program: 3 min. isothermal at 60° C then 8°/min to 160°, hold at 160 until all compounds elute.

[3] This is a minimum level at which the entire system must give recognizable mass spectra and acceptable calibration points.

[4] Sensitivity refers to either this method or direct aqueous injection GC–FID (Ref. 4,5,6).

Table 3.—*DFTPP Key Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
51	30 to 60 pct of mass 198.
68	Less than 2 pct of mass 69.
70	Less than 2 pct of mass 69.
127	40 to 60 pct of mass 198.
197	Less than 1 pct of mass 198.
198	Base peak, 100 pct relative abundance.
199	5 to 9 pct of mass 198.
275	10 to 30 pct of mass 198.
365	Greater than 1 pct of mass 198.
441	Present but less than mass 443.
442	Greater than 40 pct of mass 198.
443	17 to 23 pct of mass 442.

Table 4.—*BFB Keyt Ions and Ion Abundance Criteria*

Mass	Ion abundance criteria
50	20 to 40 pct of mass 95.
75	50 to 70 pct of mass 95.
95	Base peak, 100 pct relative abundance.
96	5 to 9 pct of mass 95.
173	Less than 1 pct of mass 95.
174	70 to 90 pct of mass 95.
175	5 to 9 pct of mass 95.
176	70 to 90 pct of mass 95.
177	5 to 9 pct of mass 95.

Table 5.—*Characteristic Ions of Volatile Organics*

Compound	EI ions				Primary ion
chloromethane	50	52	----	----	50
bromomethane	94	96	----	----	94
vinyl chloride	62	64	----	----	62
chloroethane	64	66	----	----	64
methylene chloride	49	51	84	86	84
trichlorofluoromethane	101	103	----	----	101
1,1-dichloroethene	61	96	98	----	96
bromochloromethane (SS)	49	130	128	51	128
1,1-dichloroethane	63	65	83	----	63
	85	98	100	----	----
trans-1,2-dichloroethene	61	96	98	----	96
chloroform	83	85	----	----	83
1,2-dichloroethane	62	64	98	100	98
1,1,1-trichloroethane	97	99	117	119	97
carbon tetrachloride	117	119	121	----	117
bromodichloromethane	83	85	127	129	127
1,2-dichloropropane	63	65	112	114	112
trans-1,3-dichloropropene	75	77	----	----	75
trichloroethene	95	97	130	132	130
dibromochloromethane	129	127	208	206	127
cis-1,3-dichloropropene	75	77	----	----	75
1,1,2-trichloroethane	83	85	97	----	----
	99	132	134	----	97
benzene	78	----	----	----	78
2-chloroethylvinyl ether	63	65	106	----	106
2-bromo-1-chloropropane (SS)	77	79	156	----	77
bromoform	171	173	175	250	173
	252	254	256	----	----
tetrachloroethene	129	131	164	166	164
1,1,2,2-tetrachloroethane	83	85	131	133	----
	166	168	----	----	168
1,4-dichlorobutane (SS)	55	90	92	----	55
toluene	91	92	----	----	92
chlorobenzene	112	114	----	----	112
ethylbenzene	91	106	----	----	106
acrolein	26	27	55	56	56
acrylonitrile	26	51	52	53	53

BILLING CODE 6560-01-M

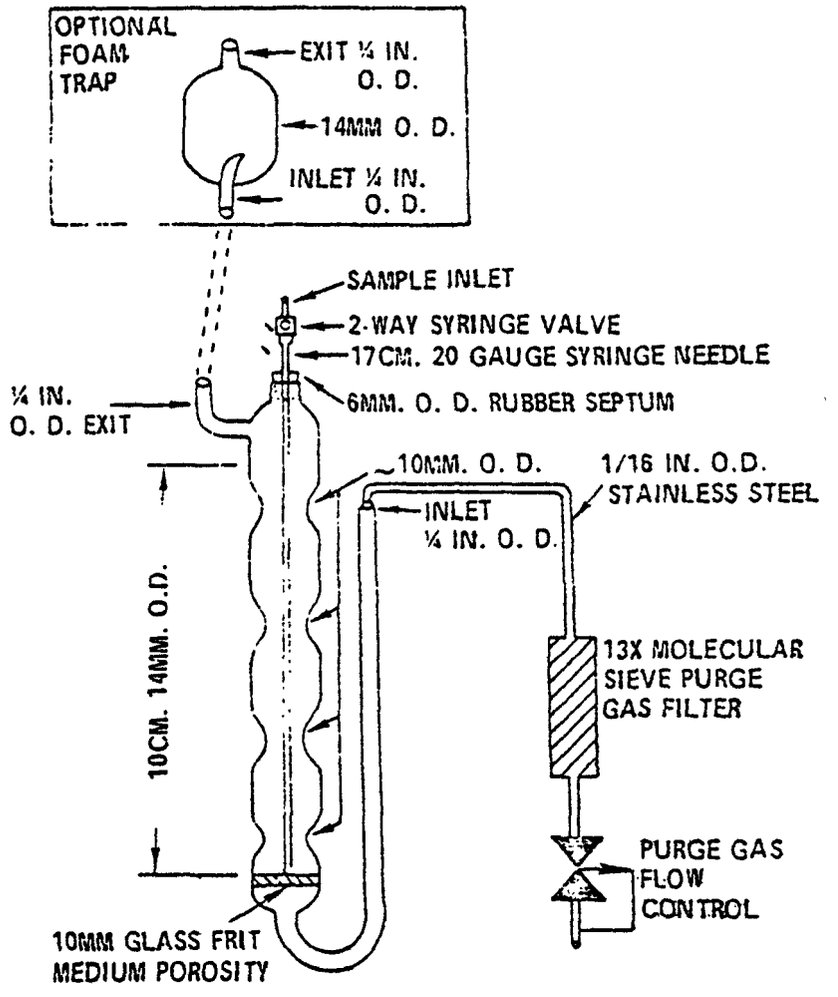

Figure 1. Purging device

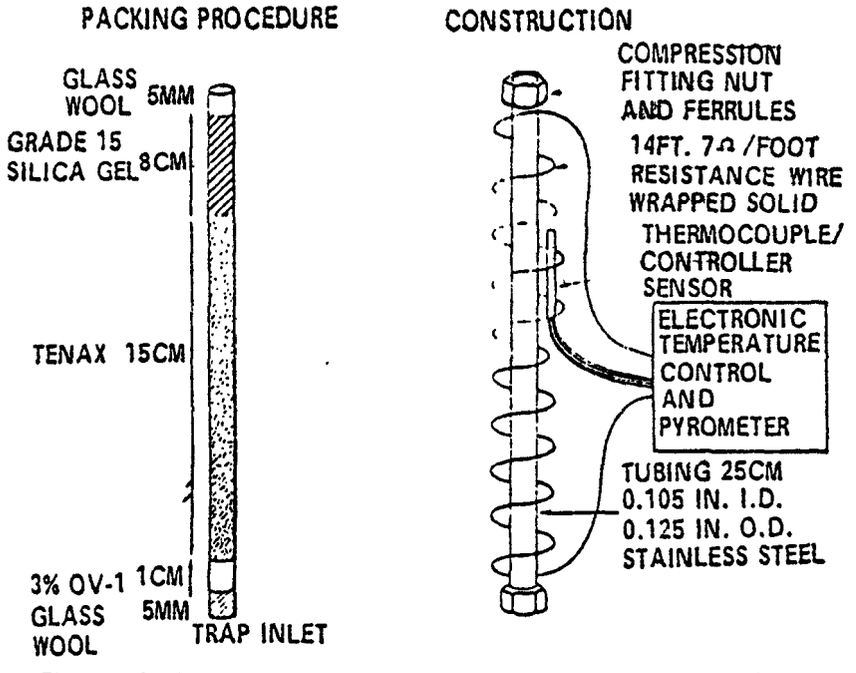

Figure 2. Trap packings and construction to include desorb capability

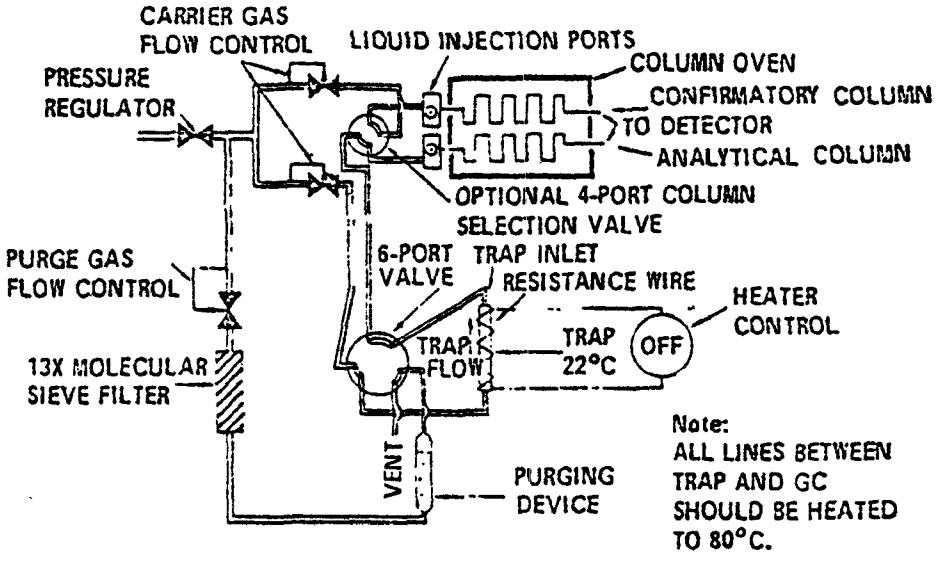

Figure 3. Schematic of purge and trap device - purge mode

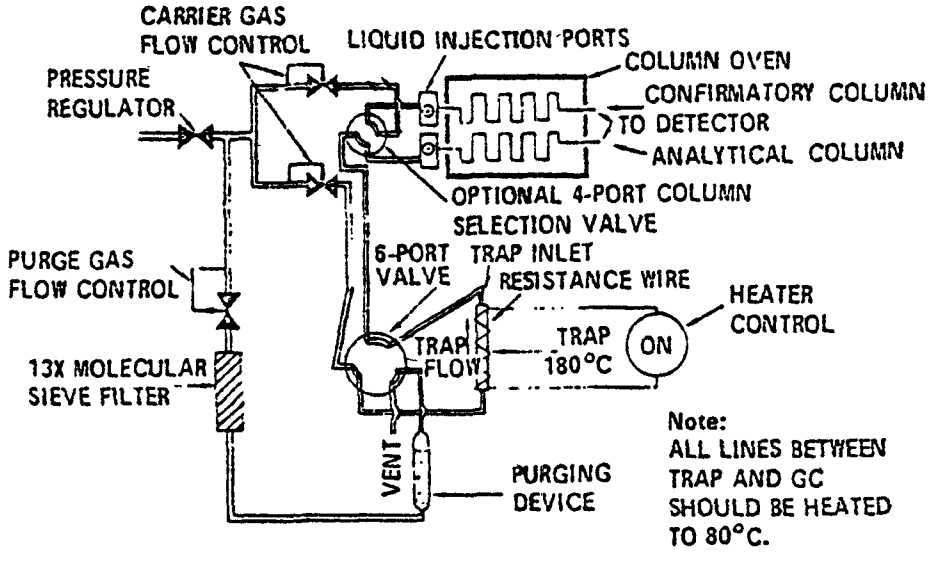

Figure 4. Schematic of purge and trap device - desorb mode

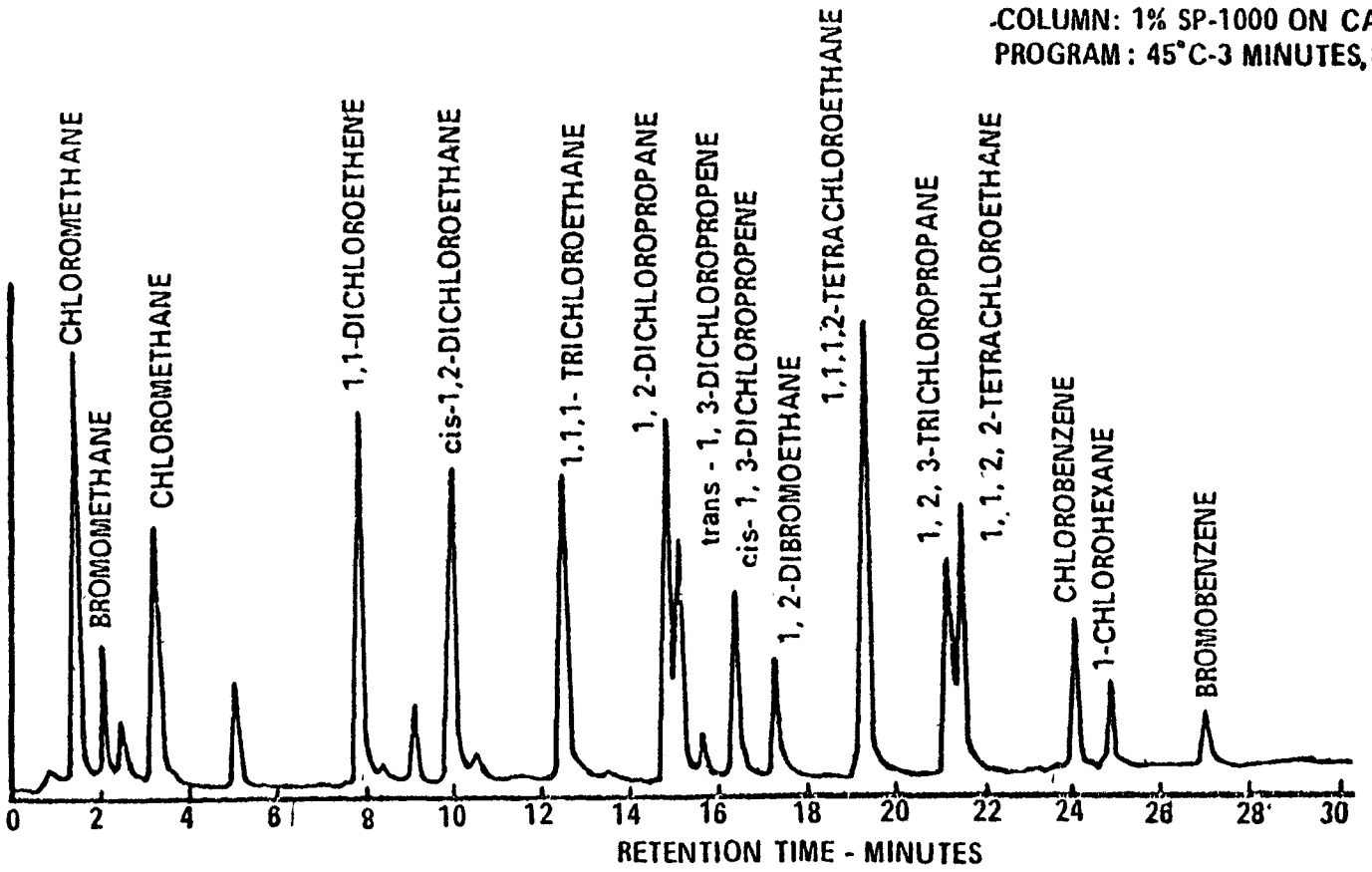

Figure 5. Gas chromatogram of volatile organics by purge and trap

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Base/Neutrals, Acids, and Pesticides—Method 625

1. *Scope and Application.*

1.1 This method covers the determination of a number of organic compounds that are solvent extractable and amenable to gas chromatography. The parameters listed in Tables 1, 2 and 3 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Tables 4, 5, and 6 represent the minimum quantity that must be injected into the system to get confirmation by the mass spectrometric method described below.

1.4 The GC/MS parts of this method are recommended for use only by analysts experienced with GC/MS or under the close supervision of such qualified persons.

2. *Summary of Method.*

2.1 A 1 to 2 liter sample of wastewater is extracted with methylene chloride using separatory funnel or continuous extraction techniques. If emulsions are a problem, continuous extraction techniques should be used. The extract is dried over sodium sulfate and concentrated to a volume of 1 ml using a Kuderna-Danish (K-D) evaporator. Chromatographic conditions are described which allow for the separation of the compounds in the extract.

2.2 Quantitative analysis is performed by GC/MS using either the internal standard or external standard technique.

3. *Interferences.*

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of chromatograms. All of these materials must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.2 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled.

3.3 The recommended analytical procedure may not have sufficient resolution to differentiate between certain isomeric pairs. These are anthracene and phenanthrene, chrysene and benzo(a)anthracene, and benzo(b)fluoranthene and benzo(k)fluoranthene. The GC retention time and mass spectral data are not sufficiently unique to make an unambiguous distinction between these compounds. Alternative techniques should be used to identify and quantify these specific compounds. See Reference 1.

4. *Apparatus and Materials.*

4.1 Sampling equipment, for discrete or composite sampling.

4.1.1 Grab sample bottle—amber glass, 1-liter to 1-gallon volume. French or Boston Round design is recommended. The container must be washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps—Threaded to fit sample bottles. Caps must be lined with Teflon. Aluminum foil may be substituted if sample is not corrosive.

4.1.3 Compositing equipment—Automatic or manual compositing system. Must incorporate glass sample containers for the collection of a minimum of 1000 ml. Sample containers must be kept refrigerated during sampling. No plastic or rubber tubing other than Teflon may be used in the system.

4.2 Separatory funnel—2000 ml, with Teflon stopcock (Ace Glass 7228-T-72 or equivalent).

4.3 Drying column—A 20 mm ID pyrex chromatographic column equipped with coarse glass frit or glass wool plug.

4.4 Kuderna-Danish (K-D) Apparatus

4.4.1 Concentrator tube—10 ml, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked. Ground glass stopper (size 19/22 joint) is used to prevent evaporation of extracts.

4.4.2 Evaporative flask—500 ml (Kontes K-57001-0500 or equivalent). Attach to concentrator tube with springs. (Kontes K-662750-0012).

4.4.3 Snyder column—three-ball macro (Kontes K503000-0232 or equivalent).

4.4.4 Snyder column—two-ball micro (Kontes K-569002-0219 or equivalent).

4.4.5 Boiling chips-extracted, approximately 10/40 mesh.

4.5 Water bath—Heated, with concentric ring cover, capable of temperature control (±2° C). The bath should be used in a hood.

4.6 Gas chromatograph—Analytical system complete with gas chromatograph capable of on-column injection and all required accessories including column supplies, gases, etc.

4.6.1 Column 1—For Base/Neutral and Pesticides a 6-foot glass column (¼ in OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 Supelcoport (or equivalent).

4.6.2 Column 2—For Acids, a 6-foot glass column (¼ in OD x 2 mm ID) packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport (or equivalent).

4.7 Mass Spectrometer—Capable of scanning from 35 to 450 a.m.u. every 7 seconds or less at 70 volts (nominal) and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when the sample is introduced through the GC inlet (Reference 2). The mass spectrometer must be interfaced with a gas chromatograph equipped with an injector system designed for splitless injection and glass capillary columns or an injector system designed for on-column injection with all-glass packed columns. All sections of the transfer lines must be glass or glass-lined and must be deactivated. (Use Sylon-CT, Supelco, Inc., or equivalent to deactivate.)

Note.—Systems utilizing a jet separator for the GC effluent are recommended since membrane separators may lose sensitivity for light molecules and glass frit separators may inhibit the elution of polynuclear aromatics. Any of these separators may be used provided that it gives recognizable mass spectra and acceptable calibration points at the limit of detection specified for each individual compound listed in Tables 4, 5, and 6.

4.8 A computer system must be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC-MS runs. There must be computer software available to allow searching any GC-MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under any specific ion plot peak is essential for quantification.

4.9 Continuous liquid-liquid extractors—Teflon or glass connecting joints and stopcocks, no lubrication. (Hershberg-Wolf Extractor—Ace Glass Co., Vineland, N.J. P/N 6841-10 or equivalent).

5. *Reagents.*

5.1 Sodium hydroxide—(ACS) 6N in distilled water.

5.2 Sulfuric acid—(ACS) 6N in distilled water.

5.3 Sodium sulfate—(ACS) granular anhydrous (rinsed with methylene chloride (20 ml/g) and conditioned at 400° C for 4 hrs.).

5.4 Methylene chloride—Pesticide quality or equivalent.

5.5 Stock standards—Obtain stock standard solutions at a concentration of 1.00 μg/μl. For example, dissolve 0.100 grams of assayed reference material in pesticide quality isooctane or other appropriate solvent and dilute to volume in a 100 ml ground glass stoppered volumetric flask. The stock solution is transferred to 15 ml Teflon lined screw cap vials, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them. Protect PNA standards from light.

6. *Calibration.*

6.1 Prepare calibration standards that contain the compounds of interest, either singly or mixed together. The standards should be prepared at concentrations that will bracket the working range of the chromatographic system (two or more orders of magnitude are suggested). If the limit of detection (Tables 4, 5, or 6) can be calculated as 20 ng injected, for example, prepare standards at 1 μg/ml, 10 μg/ml, 100 μg/ml, etc. so that injections of 1–5 μl of the calibration standards will define the linearity of the detector in the working range.

6.2 Assemble the necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in Tables 4, 5, and 6. By injecting calibration standards, establish the linear range of the analytical system and demonstrate that the analytical system meets the limits of detection requirements of Tables 4, 5, and 6. If the sample gives peak areas above the working range, dilute and reanalyze.

6.3 Internal Standard Method—The internal standard approach is acceptable for all of the semivolatile organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. 1 $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount (μg) of the internal standard.

C_s is the amount (μg) of the pollutant standard.

6.3 The relative response ratio for the pollutants should be known for at least two concentration values—20 ng injected to approximate 10 μg/l and 200 ng injected to approximate the 100 μg/l level. (Assuming 1 ml final volume and a 2 μl injection). Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response.

The response factor (RF) should be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same (20 μg) so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s), using a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed. To quantify, add the internal standard to the concentrated sample extract no more than a few minutes before injecting into the GC/MS to minimize the possibility of losses due to evaporation, adsorption, or chemical reaction. Calculate the concentration by using the previous equations with the appropriate response factor taken from the calibration curve. Either deuterated or fluorinated compounds can be used as internal standards and surrogate standards. Naphthalene-d_8, anthracene-d_{10}, pyridine-d_5, aniline-d_5, nitrobenzene-d_5, 1-fluoronaphthalene, 2-fluoronaphthalene, 2-fluorobiphenyl, 2,2'-difluorobiphenyl, and 1,2,3,4,5-pentafluorobiphenyl have been used or suggested as appropriate internal standards/surrogates for the base-neutral compounds. Phenol-d_6, pentafluorophenol, 2-perfluoromethyl phenol, and 2-fluorophenol have been used or suggested for the acid compounds. Compounds used as internal standards are not to be used as surrogate standards. The internal standard must be different from the surrogate standards.

6.5 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the limit of detection (Tables 4, 5, and 6). After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, demonstrate through the analysis of a method blank, that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected and analyzed to determine the precision of the sampling technique. Laboratory replicates should be analyzed to determine the precision of the analysis. Fortified samples should be analyzed to determine the accuracy of the analysis. Field blanks should be analyzed to check for contamination introduced during sampling and transportation.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers. Conventional sampling practices should be followed, except that the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be free of tygon and other potential sources of contamination.

8.2 The samples must be iced or refrigerated from the time of collection until extraction. Chemical preservatives should not be used in the field unless more than 24 hours will elapse before delivery to the laboratory. If the samples will not be extracted within 48 hours of collection, they must be preserved as follows:

8.2.1 If the sample contains residual chlorine, add 35 mg of sodium thiosulfate per 1 ppm of free chlorine per liter of sample.

8.2.2 Adjust the pH of the water sample to a pH of 7 to 10 using sodium hydroxide or sulfuric acid. Record the volume of acid or base used.

8.3 All samples must be extracted within 7 days and completely analyzed within 30 days of collection.

9. *Sample Extraction (Base/Neutrals, Acids, and Pesticides).*

9.1 Samples may be extracted by separatory funnel techniques or with a continuous extractor as described in Section 10. Where emulsions prevent acceptable solvent recovery with the separatory funnel technique, the analyst must use the continuous extractor.

9.2 The details of the extraction technique should be adjusted according to the sample volume. The technique described below assumes a sample

volume of 1000 ml. For volumes approximating 2-liters, the volume of extraction solvent should be adjusted to 250, 100, and 100 ml for the serial extraction of the base neutrals, and 200, 100, and 100 ml for the acids.

9.3 Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a two-liter separatory funnel. Adjust the pH of the sample with 6N NaOH to 11 or greater. Use multirange pH paper for the measurements. Proceed to Section 10 if continuous extraction is used.

9.4 Add 60 ml methylene chloride to the sample bottle, cap, and shake 30 seconds to rinse the walls. Transfer the solvent into the separatory funnel, and extract the sample by shaking the funnel for two minutes with periodic venting to release excess vapor pressure. Allow the organic layer to separate from the water phase for a minimum of ten minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, or centrifugation. (If the emulsion cannot be broken, that is, recovery is less than 80% of the added solvent corrected for the water solubility of methylene chloride, transfer the sample, solvent, and emulsion into a continuous extractor and proceed as described in Section 10). Collect the methylene chloride extract in a 250-ml Erlenmeyer flask.

9.5 Add a second 60-ml volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

9.6 Perform a third extraction in the same manner. Pour the combined extract through a drying column containing 3–4 inches of anhydrous sodium sulfate, and collect it in a 500 ml K–D flask equipped with 10 ml concentrator tube. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride. Pour this through the drying column. Seal, label as base/neutral fraction, and proceed with the acid extraction. If the extract must be stored overnight before analysis by GC/MS, it may be transferred to a 2 ml serum vial equipped with a Teflon-lined rubber septum and crimp cap.

9.7 Acid (Phenols) Extraction—Adjust the pH of the water, previously extracted for base-neutrals, with 6N H_2SO_4 to 2 or below. Serially extract with 60, 60 and 60 ml portions of distilled-in-glass methylene chloride. Collect and combine the extracts in a 250-ml Erlenmeyer flask then dry by passing through a column of anhydrous sodium sulfate. Rinse the Erlenmeyer with 20 to 40 ml of methylene chloride and pour through the drying column. Seal, label acid fraction and prepare for concentration.

9.8 Concentrate the extracts (Base/Neutrals and Acids) in a 500 ml K–D flask equipped with a 10 ml concentrator tube.

9.9 Add 1 to 2 clean boiling chips to the flask and attach a three-ball macro-Snyder column. Prewet the Snyder column by adding about 1 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid has reached an apparent volume 1 ml, remove the K–D apparatus and allow the solvent to drain for at least 10 minutes while cooling. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 ml of methylene chloride. A 5-ml syringe is recommended for this operation.

9.10 Add a clean boiling chip and attach a two-ball micro-Snyder column to the concentrator tube in 9.8. Prewet the column by adding about 0.5 ml methylene chloride through the top. Place the K–D apparatus on a warm water bath (60 to 65°C) so that the concentrator tube is partially immersed in the water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5–10 minutes. At the proper rate of distillation the balls of the column actively chatter but the chambers do not flood. When the liquid reaches an apparent volume of about 0.5 ml, remove the K–D from the water bath and allow the solvent to drain and cool for at least 10 minutes. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 ml of methylene chloride. Adjust the final volume to 1.0 ml, seal, and label as acid fraction.

9.11 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-ml graduated cylinder. Record the sample volume to the nearest 5 ml.

10. *Emulsions/Continuous Extraction.*

10.1 Place 100 to 150 ml of methylene chloride in the extractor and 200–500 ml methylene chloride in the distilling flask.

10.2 Add the aqueous sample (pH 11 or greater) to the extractor. Add blank water as necessary to operate the extractor and extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride in a 500 ml K–D evaporator flask quipped with a 10 ml concentrator tube. Seal, label as the base/neutral fraction, and concentrate as per sections 9.8 to 9.10.

10.3 Adjust the pH of the sample in the continuous extractor to 2 or below using 6N sulfuric acid. Charge a clean distilling flask with 500 ml of methylene chloride. Extract for 24 hours. Remove the distilling flask and pour the contents through a drying column containing 7 to 10 cm of anhydrous sodium sulfate. Collect the methylene chloride layer on a K–D evaporator flask equipped with a 10 ml concentrator tube. Label as the acid fraction. Concentrate as per sections 9.8 to 9.10.

11. *Calibration of the GC–MS System.*

11.1 At the beginning of each day, the mass calibration of the GC–MS system must be checked and adjusted if necessary to meet DFTPP specifications (11.3). Each day base-neutrals are measured, the column performance specification (12.1) with benzidine must be met. Each day the acids are measured, the column performance specification (13.1) with pentachlorophenol must be met. DFTPP can be mixed in solution with either of these compounds to complete two specifications with one injection, if desired.

11.2 To perform the mass calibration test of the GC–MS system, the following instrumental parameters are required:

Electron energy—70 volts (nominal).
Mass range—35 to 450 a.m.u.
Scan time—7 seconds or less.

11.3 GC–MS system calibration—Evaluate the system performance each day that it is to be used for the analysis of samples or blanks by examining the mass spectrum of DFTPP. Inject a solution containing 50 ug DFTPP and check to insure that performance criteria listed in Table 10 are met. If the system performance criteria are not met, the analyst must retune the spectrometer and repeat the performance check. The performance criteria must be met before any samples or standards may be analyzed.

12. *Gas Chromatography-Mass Spectrometry of Base/Neutral Fraction.*

12.1 At the beginning of each day that base/neutral analyses are to be performed, inject 100 nanograms of benzidine either separately or as part of a standard mixture that may also contain 50 ng of DFTPP. The tailing factor for benzidine should be less than 3. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

12.2 Establish chromatographic conditions equivalent to those in Tables 4 and 5. Included in these tables are estimated retention times and sensitivities that can be achieved by this method. Examples of the separatioins achieved by these columns are shown in Figures 1 and 3 through 7.

12.3 Program the GC/MS to operate in the Extracted Ion Current Profile (EICP) mode, and collect EICP for the three ions listed in Tables 7 and 8 for each compound being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6, using either the internal or external standard procedure.

12.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

12.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

12.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 14° C.

13. *Gas Chromatography/Mass Spectrometry of Acid Fraction.*

13.1 At the beginning of each day that acid fraction analyses are to be performed, inject 50 nanograms of pentachlorophenol either separately or as part of a standard mixture that may also contain DFTPP. The tailing factor for pentachlorophenol should be less than 5. Calculation of the tailing factor is given in Reference 2 and described in Figure 8.

13.2 Establish chromatographic conditions equivalent to those in Table 6. Included in this table are estimated retention times and sensitivities that can be achieved by this method. An example of the separation achieved by the column is shown in Figure 2.

13.3 Program the GC/MS to operate in the Extracted Ion Current Profile mode, and collect EICP for the three ions listed in Table 9 for each phenol being measured. Operating in this mode, calibrate the system response for each compound as described in Section 6 using either the internal or external standard procedure.

13.4 If the internal standard approach is being used, the analyst may not add the standard to sample extracts until immediately before injection into the instrument. Mix thoroughly.

13.5 Inject 2 to 5 μl of the sample extract. The solvent-flush technique is preferred. If external standard calibration is employed, record the volume injected to the nearest 0.05 μl. If the response for any ion exceeds the linear range of the system, dilute the extract and reanalyze.

13.6 Qualitative and quantitative measurements are made as described in Section 14. When the extracts are not being used for analysis, store them in vials with unpierced septa in the dark at 4° C.

14. *Qualitative and Quantitative Determination.*

14.1 To qualitatively identify a compound, obtain an Extracted Ion Current Profile (EICP) for the primary ion and the two other ions listed in Tables 7, 8, or 9. The criteria below must be met for a qualitative identification.

14.1.1 The characteristic ions for the compound must be found to maximize in the same or within one spectrum of each other.

14.1.2 The retention time at the experimental mass spectrum must be within ±60 seconds of the retention time of the authentic compound.

14.1.3 The ratios of the three EICP peak heights must agree within ±20% with the ratios of the relative intensities for these ions in a reference mass spectrum. The reference mass spectrum can be obtained from either a standard analyzed through the GC–MS system or from a reference library.

14.1.4 Structural isomers that have very similar mass spectra can be explicitly identified only if the resolution between the isomers in a standard mix is acceptable. Acceptable resolution is achieved if the valley height between isomers is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

14.2 In samples that contain an inordinate number of interferences the chemical ionization (CI) mass spectrum may make identification easier. In Tables 7 and 8 characteristic CI ions for most of the compounds are given. The use of chemical ionization MS to support EI is encouraged but not required.

14.3 When a compound has been identified, the quantification of that compound will be based on the integrated area from the specific ion plot of the first listed characteristic ion in Tables 7, 8 and 9. If the sample produces an interference for the first listed ion, use a secondary ion to quantify. Quantification will be done by the external or internal standard method.

14.4 Internal Standard—By adding a constant known amount of internal standard (C_{is} in μg) to every sample extract, the concentration of pollutant (C_o) is μg/l in the sample is calculated using equation 2.

Eq. 2 $$C_o = \frac{(A_s)\ (C_{is})}{(A_{is})\ (RF)\ (Vo)}$$

Where: V_o is the volume of the original sample in liters, and the other terms are defined as in Section 6.3.

14.5 External Standard—The concentration of the unknown can be calculated from the slope and intercept of the calibration curve. The unknown concentration can be determined using equation 3.

Eq. 3

$$\text{Micrograms/liter} = \text{ng/ml} = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = mass of compound from calibration curve (ng).
V_i = volume of extract injected (μl).
V_t = volume of total extract (μl).
V_s = volume of water extracted (ml).

14.6 Report all results to two significant figures. Report results in micrograms per liter (Base/Neutrals and Acids) without correction for recovery data. When duplicate and spiked samples are analyzed, all data obtained should be reported.

14.7 In order to minimize unnecessary GC–MS analysis of method blanks and field blanks, the field blank may be screened on a FID–GC equipped with the appropriate SP–2250 or SP–1240 DA columns.

15. References

1. Method 610, Polynuclear Aromatic Hydrocarbons, EMSL, Cincinnati, Ohio 45268, 1979.
2. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography—Mass Spectrometry Systems," J. W. Eichelberger, L. E. Harris and W. L. Budde, *Anal. Chem. 47*, 995–1000 (1975).

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   Volume 3—Norfolk, Virginia, March 1979
   USEPA, Effluent Guidelines Division, Washington, D.C. 20460.

Table 1.—*Base-Neutral Extractables*

Compound	STORET No.
Acenaphthene	34205
Acenaphthylene	34200
Anthracene	34220
Benzo(a)anthracene	34526
Benzo(b)fluoranthene	34230
Benzo(k)fluoranthene	34242
Benzo(a)pyrene	34247
Benzo(g,h,i)perylene	34521
Benzidine	39120
Bis(2-chloroethyl)ether	34273
Bis(2-chloroethoxy)methane	34278
Bis(2-ethylhexyl)phthalate	39100
Bis(2-chloroisopropyl)ether	34283
4-Bromophenyl phenyl ether	34636
Butyl benzyl phthalate	34292
2-Chloronaphthalene	34581
4-Chlorophenyl phenyl ether	34641
Chrysene	34320
Dibenzo(a,h)anthracene	34556
Di-n-butylphthalate	39110
1,3-Dichlorobenzene	34566
1,4-Dichlorobenzene	34571
1,2-Dichlorobenzene	34536
3,3'-Dichlorobenzidine	34631
Diethylphthalate	34336
Dimethylphthalate	34341
2,4-Dinitrotoluene	34611
2,6-Dinitrotoluene	34626
Dioctylphthalate	34596
1,2-Diphenylhydrazine	34346
Fluoranthene	34376
Fluorene	34381
Hexachlorobenzene	39700
Hexachlorobutadiene	34391
Hexachloroethane	34396
Hexachlorocyclopentadiene	34386
Indeno(1,2,3-cd)pyrene	34403
Isophorone	34408
Naphthalene	39250
Nitrobenzene	34447
N-Nitrosodimethylamine	34438
N-Nitrosodi-n-propylamine	34428
N-Nitrosodiphenylamine	34433
Phenanthrene	34461
Pyrene	34469
2,3,7,8-Tetrachlorodibenzo-p-dioxin	34675
1,2,4-Trichlorobenzene	34551

Table 2.—*Acid Extractables*

Compound	STORET No.
4-Chloro-3-methylphenol	34452
2-Chlorophenol	34586
2,4-Dichlorophenol	34601

Table 2.—*Acid Extractables*—Continued

Compound	STORET No.
2,4-Dimethylphenol	34606
2,4-Dinitrophenol	34616
2-Methyl-4,6-dinitrophenol	34657
2-Nitrophenol	34591
4-Nitrophenol	34646
Pentachlorophenol	39094
Phenol	34694
2,4,6-Trichlorophenol	34621

Table 3.—*Pesticide Extractables*

Compound	STORET No.
Aldrin	39330
a-BHC	39337
b-BHC	39338
d-BHC	39340
g-BHC	34259
Chlordane	39350
4,4'-DDD	39310
4,4'DDE	39320
4,4'DDT	39300
Dieldrin	39380
Endosulfan I	34361
Endosulfan II	34356
Endosulfan Sulfate	34351
Endrin	39390
Endrin Aldehyde	34366
Heptachlor	39410
Heptachlor Epoxide	39420
Toxaphene	39400
PCB-1016	34671
PCB-1221	39488
PCB-1232	39492
PCB-1242	39496
PCB-1248	39500
PCB-1254	39504
PCB-1260	39508

Table 4—*Gas Chromatography of Base/Neutral Extractables*

Compound	Retention time # (min.)	Limit of detection ## ng injected	Limit of detection ## µg/l
1,3-Dichlorobenzene	7.4	20	10
1,4-Dichlorobenzene	7.8	20	10
Hexachloroethane	8.4	20	10
Bis(2-chloroethyl)ether	8.4	20	10
1,2-Dichlorobenzene	8.4	20	10
Bis(2-chloroisopropyl)ether	9.3	20	10
N-nitroso-di-n-propyl amine	----------	20	10
Nitrobenzene	11.1	20	10
Hexachlorobutadiene	11.4	20	10
1,2,4-Trichlorobenzene	11.6	20	10
Isophorone	11.9	20	10
Naphthalene	12.1	20	10
Bis(2-chloroethoxy) methane	12.2	20	10
Hexachlorocyclopentadiene	13.9	20	10
2-Chloronaphthalene	15.9	20	10
Acenaphthylene	17.4	20	10
Acenaphthene	17.8	20	10
Dimethyl phthalate	18.3	20	10
2,6-Dinitrotoluene	18.7	20	10
Fluorene	19.5	20	10
4-Chlorophenyl phenyl ether	19.5	20	10
2,4-Dinitrotoluene	19.8	20	10
1,2-Diphenyl hydrazine*	20.1	20	10
Diethyl phthalate	20.1	20	10
N-nitrosodiphenyl amine**	20.5	20	10
Hexachlorobenzene	21.0	20	10
4-Bromophenyl phenyl ether	21.2	20	10
Phenanthrene	22.8	20	10
Anthracene	22.8	20	10
Di-n-butyl phthalate	24.7	20	10
Fluoranthene	26.5	20	10
Pyrene	27.3	20	10
Benzidine	28.5	20	10
Butyl benzyl phthalate	29.9	20	10
Bis(2-ethylhexyl) phthalate	30.6	20	10
Chrysene	31.5	20	10

Table 4—*Gas Chromatography of Base/Neutral Extractables*—Continued

Compound	Retention time # (min.)	Limit of detection ## ng injected	Limit of detection ## µg/l
Benzo(a)anthracene	31.5	20	10
3,3'-Dichlorobenzidine	32.2	20	10
Di-n-octyl phthalate	32.5	20	10
Benzo(b)fluoranthene	34.9	20	10
Benzo(k)fluoranthene	34.9	20	10
Benzo(a)pyrene	36.4	20	10
Indeno(1,2,3-c,d)pyrene	42.7	50	25
Dibenzo(a,h)anthracene	43.2	50	25
Benzo(g,h,i)perylene	45.1	50	25
N-Nitrosodimethylamine			
Bis(chloromethyl)ether			
2,3,7,8-Tetrachlorodibenzo-p-dioxin			

#Six foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per min to 270° C. Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

##This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 µl injection of a one-liter sample that has been extracted and concentrated to a volume of 1.0 mL)

*Detected as azobenzene.

**Detected as diphenylamine.

Table 5.—*Gas Chromatography of Pesticide Extractables*

Compound	Retention time (min)*	Limit of detection# ng injected	Limit of detection# µg/l
a-bhc	21.1	40	10
g-bhc	22.4	40	10
b-bhc	23.4	40	10
Heptachlor	23.4	40	10
d-bhc	23.7	40	10
Aldrin	24.0	40	10
Heptachlor epoxide	25.6	40	10
Endosulfan I	26.4	40	10
Dieldrin	27.2	40	10
4,4'-DDE	27.2	40	10
Endrin	27.9	40	10
Endosulfan II	28.6	40	10
4,4'-DDD	28.6	40	10
4,4'-DDT	29.3	40	10
Endosulfan sulfate	29.8	40	10
Chlordane	19 to 30		
Toxaphene	25 to 34		
PCB-1242	20 to 32		
PCB-1254	23 to 32		

*6 foot glass column (¼ in. OD x 2 mm ID) packed with 3% SP-2250 coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: Isothermal for 4 minutes at 50° C, then 8° per minute to 270° Hold at 270° C for 30 minutes. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 4 µl injection of a one-liter sample that has been extracted and concentrated to a volume of 1.0 mL

Table 6.—*Gas Chromatography of Acid Extractables*

Compound	Retention time* (min)	Limit of detection# ng injected	Limit of detection# µg/l
2-Chlorophenol	5.9	50	25
2-Nitrophenol	6.4	50	25
Phenol	8.0	50	25
2,4-Dimethylphenol	9.4	50	25
2,4-Dichlorophenol	9.8	50	25
2,4,6-Trichlorophenol	11.8	50	25
4-Chloro-3-methylphenol	13.2	50	25
2,4-Dinitrophenol	15.9	500	250

Table 6.—*Gas Chromatography of Acid Extractables*—Continued

Compound	Retention time* (min)	Limit of detection#	
		ng injected	µg/l
2-Methyl-4,6-dinitrophenol	16.2	500	250
Pentachlorophenol	17.5	50	25
4-Nitrophenol	20.3	50	25

*6 foot glass column (¼ in. OD x 2 mm ID) Packed with 1% SP-1240 DA coated on 100/120 mesh Supelcoport. Carrier gas: helium at 30 ml per min. Temperature program: 2 min isothermal at 70°, then 8° per min to 200° C. If desired, capillary or SCOT columns may be used.

#This is a minimum level at which the entire analytical system must give mass spectral confirmation. (Nanograms injected is based on a 2 µl injection of a one liter sample that has been extracted and concentrated to 1.0 ml.)

Table 7.—*Base/Neutral Extractables Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
1,3-Dichlorobenzene	146	148	113	146	148	150
1,4-Dichlorobenzene	146	148	113	146	148	150
Hexachloroethane	117	201	199	199	201	203
Bis(2-chloroethyl) ether	93	63	95	63	107	109
1,2-Dichlorobenzene	146	148	113	146	148	150
Bis(2-chloroisopropyl) ether	45	77	79	77	135	137
N-Nitrosodipropyl amine	130	42	101	.....	.....	.....
Isophorone	82	95	138	139	167	178
Nitrobenzene	77	123	65	124	152	164
Hexachlorobutadiene	225	223	227	223	225	227
1,2,4-Trichlorobenzene	180	182	145	181	183	209
Naphthalene	128	129	127	129	157	169
Bis(2-chloroethoxy) methane	93	95	123	65	107	137
Hexachlorocyclopentadiene	237	235	272	235	237	239
2-Chloronaphthalene	162	164	127	163	191	203
Acenaphthylene	152	151	153	152	153	181
Acenaphthene	154	153	152	154	155	183
Dimethyl phthalate	63	194	164	151	163	164
2,6-Dinitrotoluene	165	63	121	83	211	223
Fluorene	166	165	167	166	167	195
4-Chlorophenyl phenyl ether	204	206	141	.....	.....	.....
2,4-Dinitrotoluene	165	89	163	183	211	223
1,2-Diphenylhydrazine[1]	77	93	105	185	213	225
Diethylphthalate	149	177	150	177	223	251
N-Nitrosodiphenylamine[2]	169	168	167	169	170	198
Hexachlorobenzene	284	142	249	284	286	288
4-Bromophenyl phenyl ether	248	250	141	249	251	277
Phenanthrene	178	179	176	178	179	207
Anthracene	178	179	176	178	179	207
Dibutyl phthalate	149	150	104	149	205	279
Fluoranthene	202	101	100	203	231	243
Pyrene	202	101	100	203	231	243
Benzidine	184	92	185	185	213	225
Butyl benzyl phthalate	149	91	.....	149	299	327
Bis(2-ethyl hexyl) phthalate	149	167	279	149	.....	.....
Chrysene	228	226	229	228	229	257
Benzo(a)anthracene	228	229	226	228	229	257
3,3'-Dichlorobenzidine	252	254	126	.....	.....	.....
Dioctyl phthalate	149	.....	.....	.....	.....	.....
Benzo(b)fluoranthene	252	253	125	252	253	281
Benzo(k)fluoranthene	252	253	125	252	253	281
Benzo(a)pyrene	252	253	125	252	253	281
Indeno(1,2,3-c,d)pyrene	276	138	277	276	277	305
Dibenzo(a,h)anthracene	278	139	279	278	279	307
Benzo(g,h,i)perylene	276	138	277	276	277	305
N-nitrosodimethyl amine	42	74	44	.....	.....	.....
Bis(chloromethyl) ether	45	49	51	.....	.....	.....
2,3,7,8-Tetrachlorodibenzo-p-dioxin	.....	322	320	59	.....	.....
Deuterated anthracene(d-10)[3]	188	94	80	189	217	.....

[1] Detected as azobenzene.
[2] Detected as diphenylamine.
[3] Suggested internal standard.

Table 8.—*Pesticides Characteristic Ions*

Compound	Characteristic ions electron impact		
a-BHC	183	181	109
g-BHC	183	181	109
b-BHC	181	183	109
heptachlor	100	272	274
d-BHC	183	109	181
aldrin	66	263	220
heptachlor epoxide	353	355	351
endosulfan I	201	283	278
dieldrin	79	263	279
4,4'-DDE	246	248	176
4,4'-DDD	235	165	237
endrin	81	263	82
endosulfan II	201	283	278
4,4'-DDT	235	237	165
endosulfan sulfate	272	387	422
chlordane [1]	373	375	377
toxaphene [2]	231	233	235
PCB-1242 [2]	224	260	294
PCB-1254 [2]	294	330	362

[1] Characteristic of alpha and gamma forms of chlordane.
[2] These compounds are mixtures of various isomers.

Table 9.—*Acid Extractable Characteristic Ions*

Compound	Characteristic ions					
	Electron impact			Chemical ionization (methane)		
2-Chlorophenol	128	64	130	129	131	157
2-Nitrophenol	139	65	109	140	168	122
Phenol	94	65	66	95	123	135
2,4-Dimethylphenol	122	107	121	123	151	163
2,4-Dicholorphenol	162	164	98	163	165	167
2,4,6-Trichlorophenol	196	198	200	197	199	201
4-Chloro-3-methyl phenol	142	107	144	143	171	183
2,4-Dinitrophenol	184	63	154	185	213	225
2-Methyl-4,6-dinitrophenol	198	182	77	199	227	239
Pentachlorophenol	266	264	268	267	265	269
4-Nitrophenol	65	139	109	140	168	122
Anthracene (d-10) [1]	188	94	80	189	217	

[1] Suggested internal standard.

Table 10.—*DFTPP Key Ions and Ion Abundance Criteria*

	Ion abundance criteria
Mass:	
51	30 to 60 percent of mass 198.
68	Less than 2 percent of mass 69.
70	Less than 2 percent of mass 69.
127	40 to 60 percent of mass 198.
197	Less than 1 percent of mass 198.
198	Base peak, 100 percent relative abundance.
199	5 to 9 percent of mass 198.
275	10 to 30 percent of mass 198.
365	Greater than 1 percent of mass 198.
441	Present but less than mass 443.
442	Greater than 40 percent of mass 198.
443	17 to 23 percent of mass 442.

BILLING CODE 6560-01-M

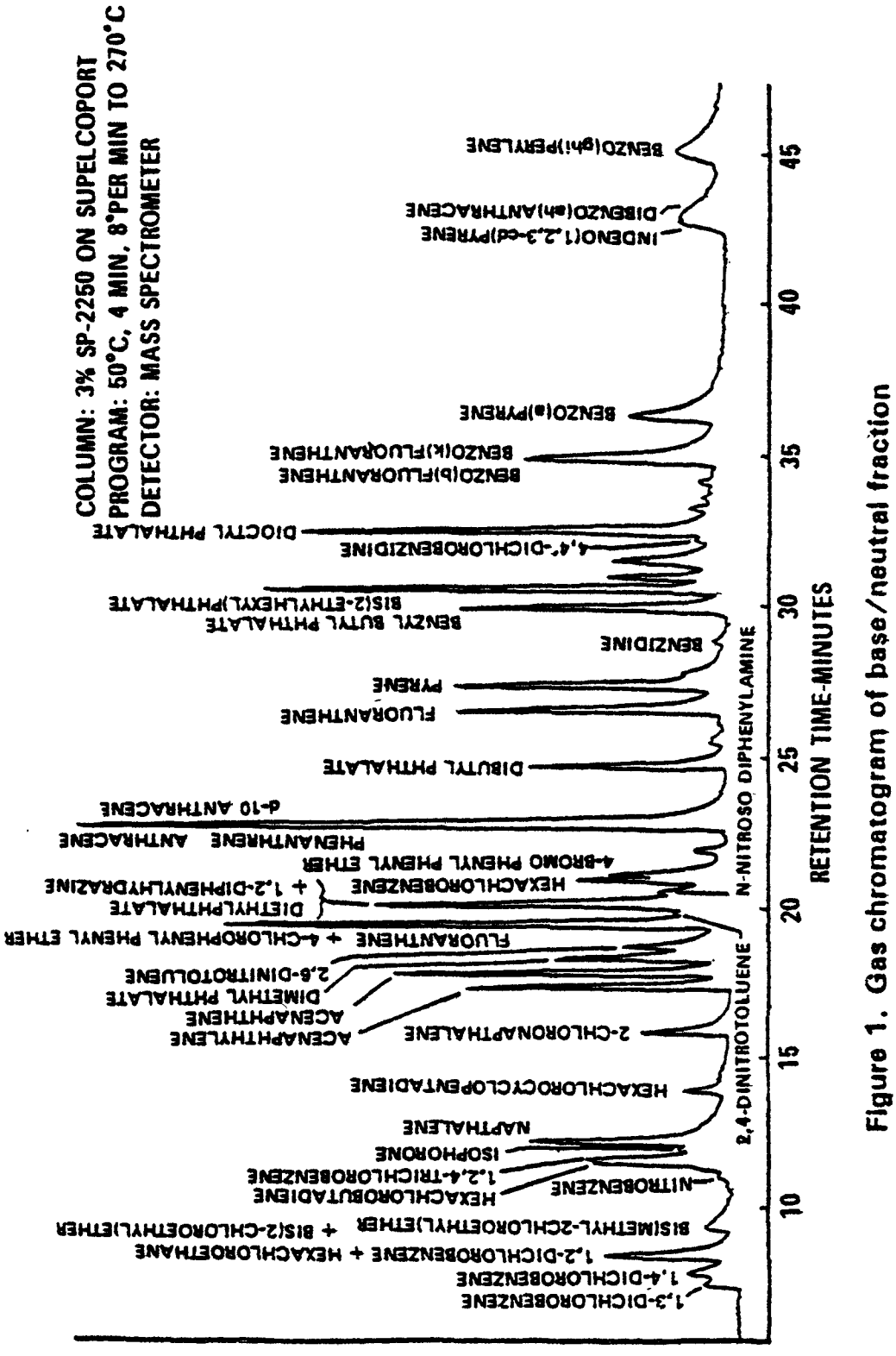


Figure 1. Gas chromatogram of base/neutral fraction

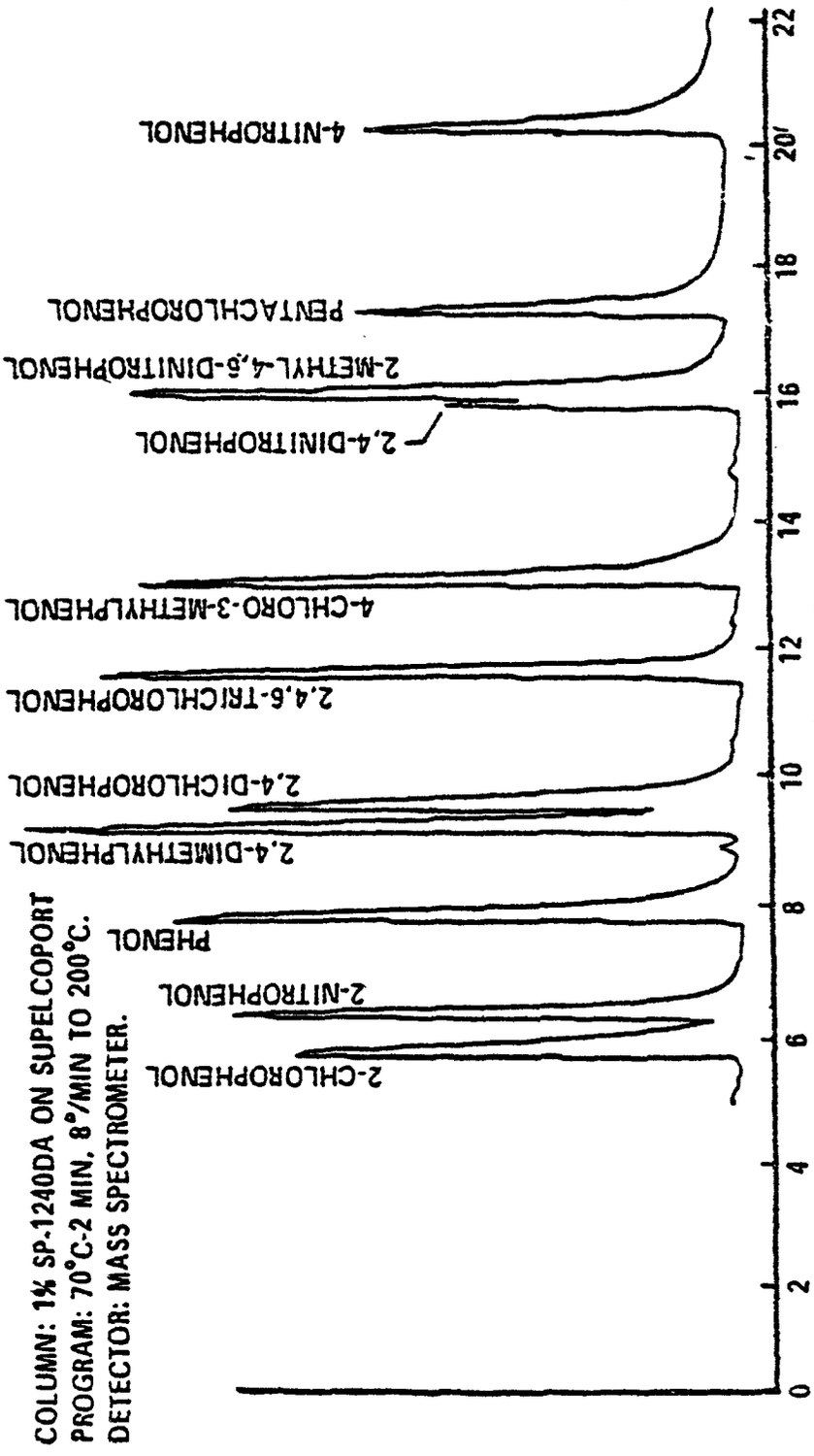


Figure 2. Gas chromatogram of acid fraction

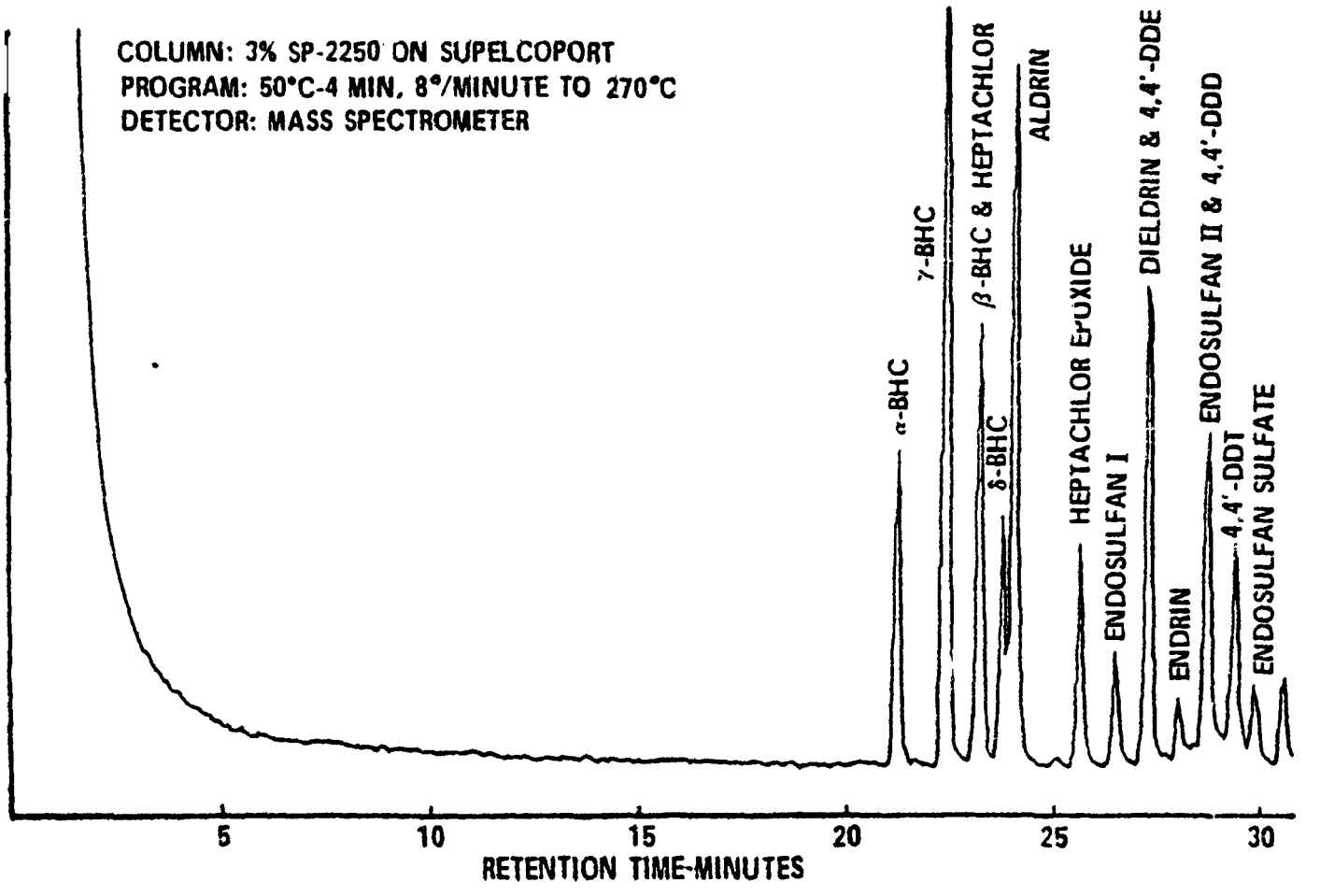


Figure 3. Gas chromatogram of pesticide fraction

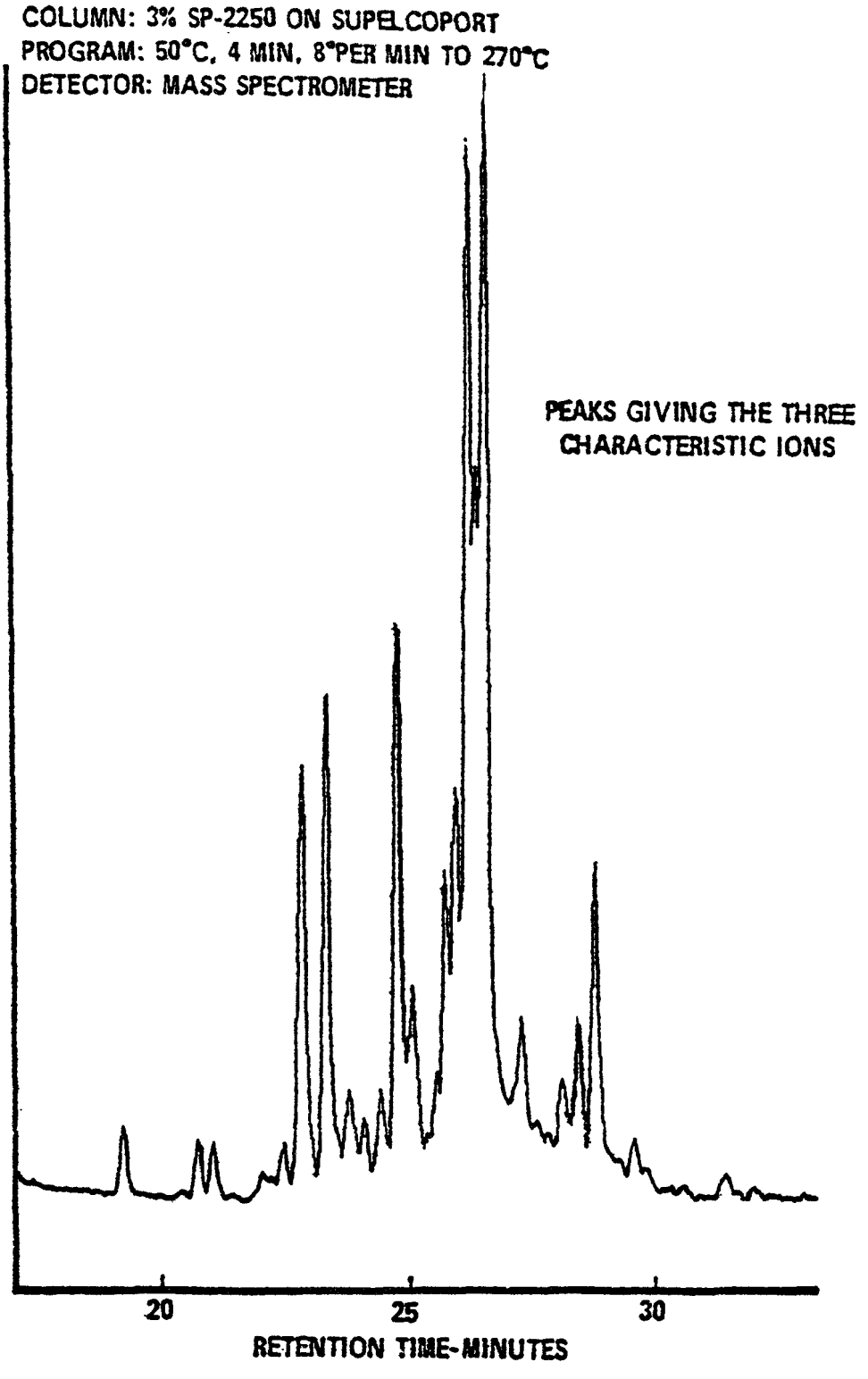


Figure 4. Gas chromatogram of chlordane

BILLING CODE 6560-01-C

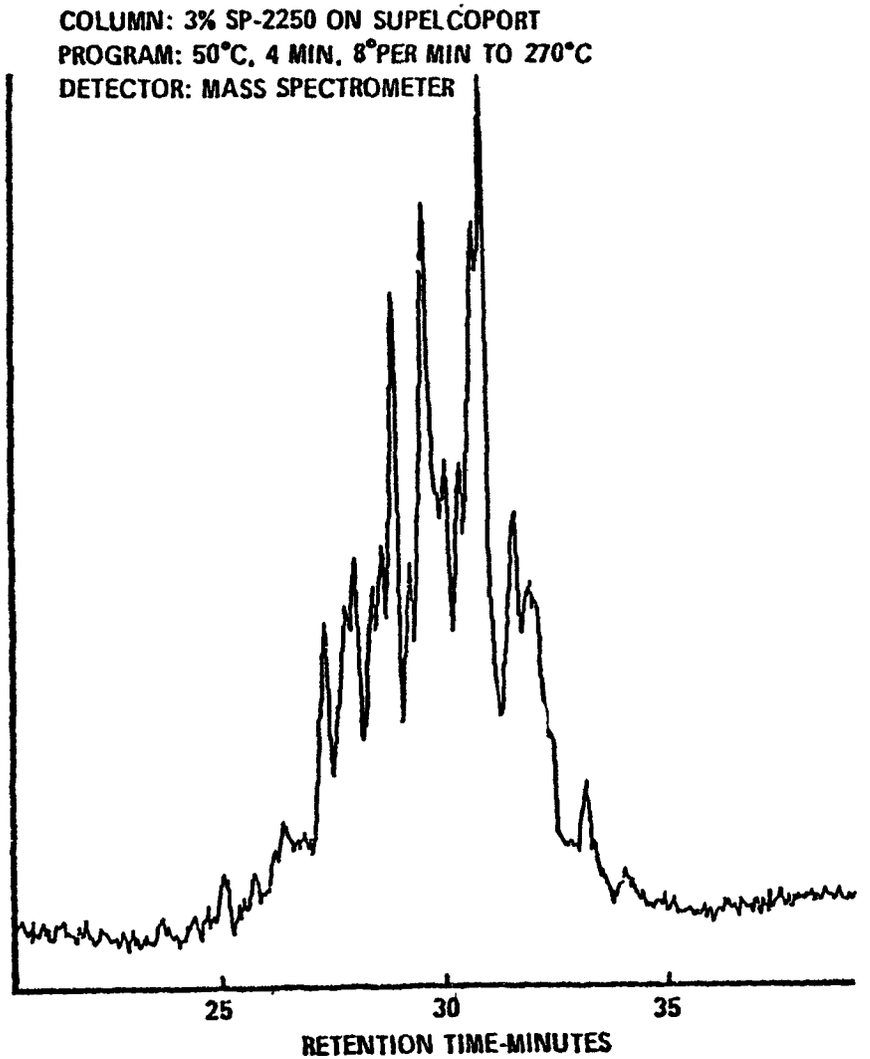


Figure 5. Gas chromatogram of toxaphene

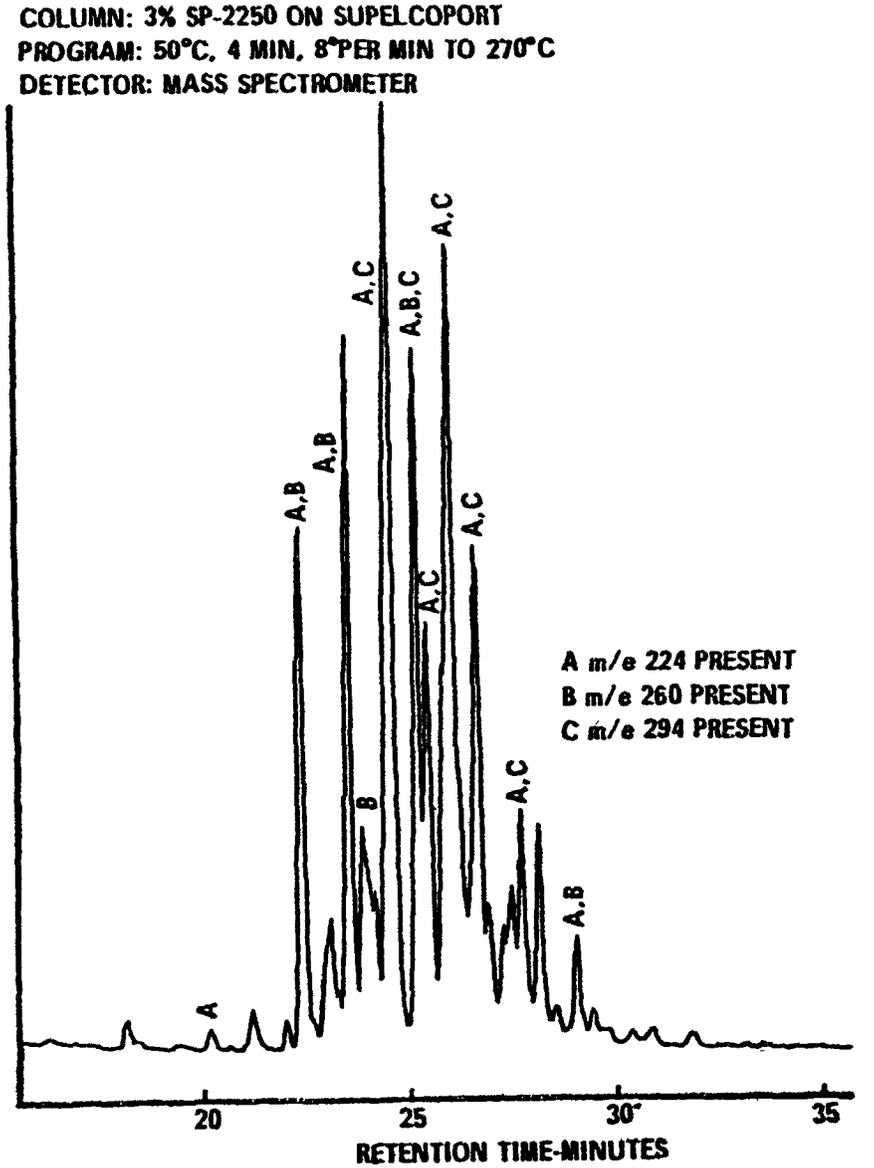


Figure 6. Gas chromatogram of Arochlor 1248

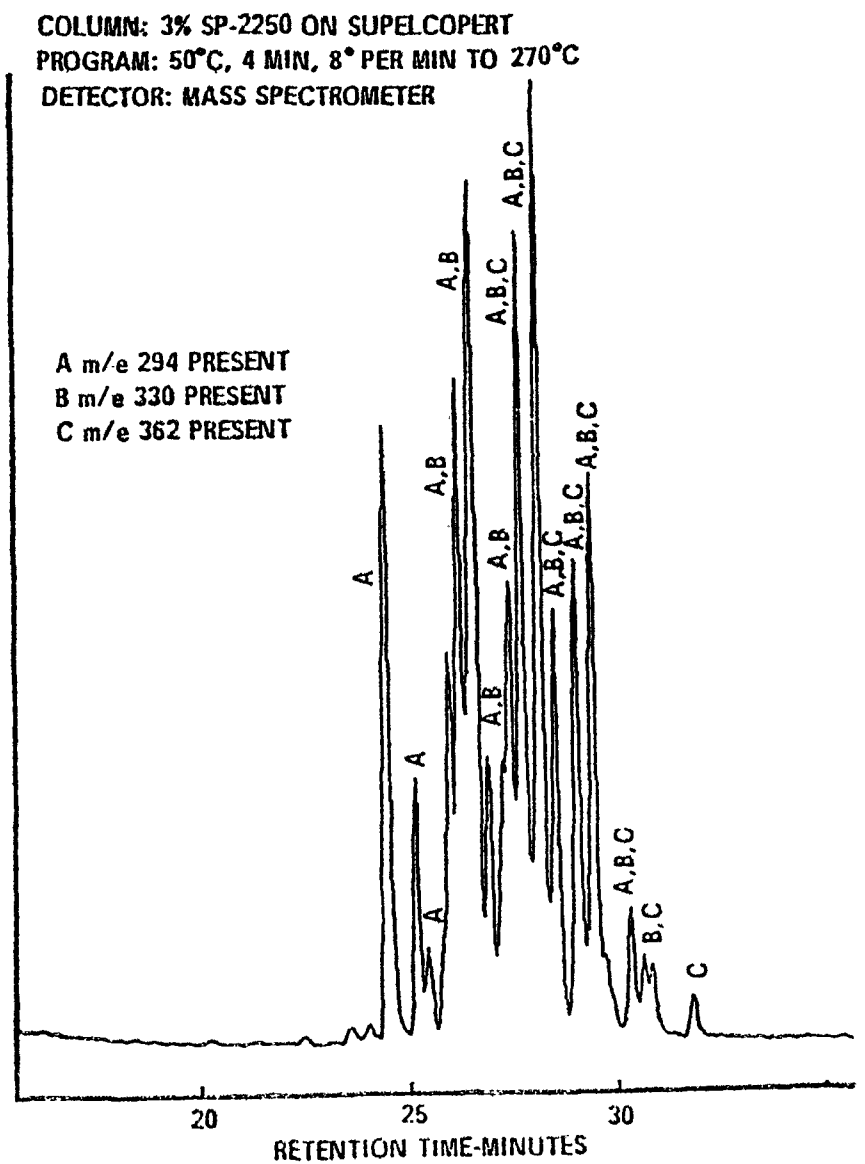
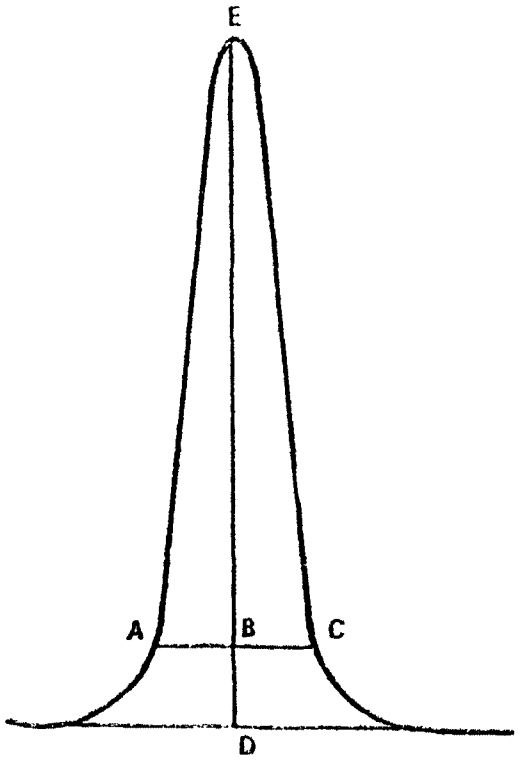


Figure 7. Gas chromatogram of Arochlor 1254

BILLING CODE 6560-01-C



$$\text{TAILING FACTOR} = \frac{BC}{AB}$$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

$$\text{Therefore: Tailing Factor} = \frac{12}{11} = 1.1$$

Figure 1. Tailing factor calculation