

SW8463C

**TEST METHODS FOR EVALUATING
SOLID WASTE, PHYSICAL/CHEMICAL
METHODS, SW-846, 3RD EDITION,**

PROPOSED UPDATE II



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PROPOSED UPDATE II

**THIS PACKET CONTAINS THE OFFICIAL PROPOSED UPDATE II FOR
TEST METHODS FOR EVALUATING SOLID WASTE, PHYSICAL/CHEMICAL
METHODS, SW-846, 3RD EDITION**

- **Table of Contents**
- **Proposed Methods for Update II, dated November 1992**
- **Proposed Chapters Two, Three, Four, and Seven**

**Remove ALL previously distributed colored sheets of
updates to SW-846.**

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N Indicates a new method
T Indicates a total revision

ABSTRACT

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides test procedures and guidance which are recommended for use in conducting the evaluations and measurements needed to comply with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580. These methods are approved by the U.S. Environmental Protection Agency for obtaining data to satisfy the requirements of 40 CFR Parts 122 through 270. This manual presents the state-of-the-art in routine analytical testing adapted for the RCRA program. It contains procedures for field and laboratory quality control, sampling, determining hazardous constituents in wastes, determining the hazardous characteristics of wastes (toxicity, ignitability, reactivity, and corrosivity), and for determining physical properties of wastes. It also contains guidance on how to select appropriate methods.

The hazardous waste regulations under Subtitle C of the Resource Conservation and Recovery Act (RCRA) require that specific testing methods described in this manual be employed for certain applications. The following sections of 40 CFR require the use of SW-846 methods:

260.22(d)(1)(i) - Submission of data in support of petitions to exclude a waste produced at a particular facility (delisting petitions).

261.22(a) - Evaluation of wastes against the Corrosivity Characteristic (corrosivity).

261.24(a) - Evaluation of wastes against the Extraction Procedure Toxicity Characteristic (mobility of toxic species).

264.314(c) and 265.314(d) - Evaluation of wastes to determine if free liquid is a component of the waste (free liquid).

270.62(b)(2)(i)(C) - Analysis of wastes prior to conducting a trial burn in support of an application for a hazardous waste incineration permit (incinerator permit).

Disclaimer

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

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Method Number Third Edition	Chapter Number Third Edition	Method Number Second Edition	Current Revision Number
0010	Ten	None (new method)	0
0020	Ten	None (new method)	0
0030	Ten	None (new method)	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	1 (PR)
1320	Six	None (new method)	0
1330	Six	None (new method)	1 (PR)
3005	Three	None (new method)	1 (PR)
3010	Three	3010	1 (PR)
3020	Three	3020	1 (PR)
3040	Three	3040	0
3050	Three	3050	1 (PR)
3500	Four (4.2.1)	None (new method)	1 (PR)
3510	Four (4.2.1)	3510	1 (PR)
3520	Four (4.2.1)	3520	1 (PR)
3540	Four (4.2.1)	3540	1 (PR)
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	1 (PR)
3610	Four (4.2.2)	None (new method)	0
3611	Four (4.2.2)	3570	0
3620	Four (4.2.2)	None (new method)	0
3630	Four (4.2.2)	None (new method)	0
3640	Four (4.2.2)	None (new method)	0
3650	Four (4.2.2)	3530	1
3660	Four (4.2.2)	None (new method)	0
3810	Four (4.4)	5020	0
3820	Four (4.4)	None (new method)	0
5030	Four (4.2.1)	5030	1 (PR)
5040	Four (4.2.1)	None (new method)	0
6010	Three	None (new method)	1
7000	Three	None (new method)	1 (PR)
7020	Three	None (new method)	0

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Method Number Third Edition	Chapter Number Third Edition	Method Number Second Edition	Current Revision Number
7040	Three	7040	0
7041	Three	7041	0
7060	Three	7060	0
7061	Three	7061	1 (PR)
7080	Three	7080	0
7081	Three	7081	0
7090	Three	7090	0
7091	Three	7091	0
7130	Three	7130	0
7131	Three	7131	0
7140	Three	None (new method)	0
7190	Three	7190	0
7191	Three	7191	0
7195	Three	7195	0
7196	Three	7196	1 (PR)
7197	Three	7197	0
7198	Three	None (new method)	0
7200	Three	None (new method)	0
7201	Three	None (new method)	0
7210	Three	None (new method)	0
7211	Three	7211	0
7380	Three	None (new method)	0
7381	Three	7381	0
7420	Three	7420	0
7421	Three	7421	0
7430	Three	None (new method)	0
7450	Three	None (new method)	0
7460	Three	None (new method)	0
7461	Three	7461	0
7470	Three	7470	0
7471	Three	7471	0
7480	Three	None (new method)	0
7481	Three	None (new method)	0
7520	Three	7520	0
7550	Three	None (new method)	0

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Method Number Third Edition	Chapter Number Third Edition	Method Number Second Edition	Current Revision Number
7610	Three	None (new method)	0
7740	Three	7740	0
7741	Three	7741	0
7760	Three	7760	1
7761	Three	7761	0
7770	Three	None (new method)	0
7780	Three	None (new method)	0
7840	Three	None (new method)	0
7841	Three	None (new method)	0
7870	Three	None (new method)	0
7910	Three	None (new method)	0
7911	Three	None (new method)	0
7950	Three	None (new method)	0
7951	Three	7951	0
8000	Four (4.3.1)	None (new method)	1 (PR)
8010	Four (4.3.1)	8010	1 (PR)
8011	Four (4.3.1)	None (new method)	0
8015	Four (4.3.1)	8015	1 (PR)
8020	Four (4.3.1)	8020	0
8021	Four (4.3.1)	None (new method)	0
8030	Four (4.3.1)	8030	1 (PR)
8040	Four (4.3.1)	8040	1 (PR)
8060	Four (4.3.1)	8060	0
8070	Four (4.3.1)	None (new method)	0
8080	Four (4.3.1)	8080	0
8090	Four (4.3.1)	8090	0
8100	Four (4.3.1)	8100	0
8110	Four (4.3.1)	None (new method)	0
8120	Four (4.3.1)	8120	1 (PR)
8140	Four (4.3.1)	8140	0
8141	Four (4.3.1)	None (new method)	0
8150	Four (4.3.1)	8150	1 (PR)
8240	Four (4.3.2)	8240	1 (PR)
8250	Four (4.3.2)	8250	1 (PR)
8260	Four (4.3.2)	None (new method)	0

METHOD INDEX AND CONVERSION TABLE
(Continued)

Method Number Third Edition	Chapter Number Third Edition	Method Number Second Edition	Current Revision Number
8270	Four (4.3.2)	8270	1 (PR)
8280	Four (4.3.2)	None (new method)	0
8310	Four (4.3.3)	8310	0
9010	Five	9010	1
9020	Five	9020	0
9021	Five	None (new method)	0
9022	Five	None (new method)	0
9030	Five	9030	1
9031	Five	None (new method)	0
9035	Five	None (new method)	0
9036	Five	None (new method)	0
9038	Five	None (new method)	0
9040	Six	9040	0
9041	Six	None (new method)	0
9045	Six	None (new method)	0
9050	Six	None (new method)	0
9060	Five	None (new method)	0
9065	Five	None (new method)	0
9066	Five	None (new method)	0
9067	Five	None (new method)	0
9070	Five	None (new method)	0
9071	Five	None (new method)	0
9080	Six	None (new method)	0
9081	Six	None (new method)	0
9090	Six	None (new method)	1 (PR)
9095	Six	None (new method)	0
9100	Six	None (new method)	0
9131	Five	None (new method)	0
9132	Five	None (new method)	0
9200	Five	None (new method)	0
9250	Five	None (new method)	0
9251	Five	None (new method)	0
9252	Five	None (new method)	0
9310	Six	None (new method)	0
9315	Six	None (new method)	0
9320	Five	None (new method)	0

METHOD INDEX AND CONVERSION TABLE
(Continued)

Method Number Third Edition	Chapter Number Third Edition	Method Number Second Edition	Current Revision Number
HCN Test Method	Seven	None (new method)	1 (PR)
H ₂ S Test Method	Seven	None (new method)	0

(PR) Indicates a Partial Revision

CHAPTER ONE

QUALITY CONTROL

1.1 INTRODUCTION

Appropriate use of data generated under the great range of analytical conditions encountered in RCRA analyses requires reliance on the quality control practices incorporated into the methods and procedures. The Environmental Protection Agency generally requires using approved methods for sampling and analysis operations fulfilling regulatory requirements, but the mere approval of these methods does not guarantee adequate results. Inaccuracies can result from many causes, including unanticipated matrix effects, equipment malfunctions, and operator error. Therefore, the quality control component of each method is indispensable.

The data acquired from quality control procedures are used to estimate and evaluate the information content of analytical data and to determine the necessity or the effect of corrective action procedures. The means used to estimate information content include precision, accuracy, detection limit, and other quantifiable and qualitative indicators.

1.1.1 Purpose of this Chapter

This chapter defines the quality control procedures and components that are mandatory in the performance of analyses, and indicates the quality control information which must be generated with the analytical data. Certain activities in an integrated program to generate quality data can be classified as management (QA) and other as functional (QC). The presentation given here is an overview of such a program.

The following sections discuss some minimum standards for QA/QC programs. The chapter is not a guide to constructing quality assurance project plans, quality control programs, or a quality assurance organization. Generators who are choosing contractors to perform sampling or analytical work, however, should make their choice only after evaluating the contractor's QA/QC program against the procedures presented in these sections. Likewise, laboratories that sample and/or analyze solid wastes should similarly evaluate their QA/QC programs.

Most of the laboratories who will use this manual also carry out testing other than that called for in SW-846. Indeed, many user laboratories have multiple mandates, including analyses of drinking water, wastewater, air and industrial hygiene samples, and process samples. These laboratories will, in most cases, already operate under an organizational structure that includes QA/QC. Regardless of the extent and history of their programs, the users of this manual should consider the development, status, and effectiveness of their QA/QC program in carrying out the testing described here.

1.1.2 Program Design

The initial step for any sampling or analytical work should be strictly to define the program goals. Once the goals have been defined, a program

must be designed to meet them. QA and QC measures will be used to monitor the program and to ensure that all data generated are suitable for their intended use. The responsibility of ensuring that the QA/QC measures are properly employed must be assigned to a knowledgeable person who is not directly involved in the sampling or analysis.

One approach that has been found to provide a useful structure for a QA/QC program is the preparation of both general program plans and project-specific QA/QC plans.

The program plan for a laboratory sets up basic laboratory policies, including QA/QC, and may include standard operating procedures for specific tests. The program plan serves as an operational charter for the laboratory, defining its purposes, its organization and its operating principles. Thus, it is an orderly assemblage of management policies, objectives, principles, and general procedures describing how an agency or laboratory intends to produce data of known and accepted quality. The elements of a program plan and its preparation are described in QAMS-004/80 (see References, Step 1.6).

Project-specific QA/QC plans differ from program plans in that specific details of a particular sampling/analysis program are addressed. For example, a program plan might state that all analyzers will be calibrated according to a specific protocol given in written standard operating procedures for the laboratory (SOP), while a project plan would state that a particular protocol will be used to calibrate the analyzer for a specific set of analyses that have been defined in the plan. The project plan draws on the program plan or its basic structure and applies this management approach to specific determinations. A given agency or laboratory would have only one quality assurance program plan, but would have a quality assurance project plan for each of its projects. The elements of a project plan and its preparation are described in QAMS/005/80 (see References, Step 1.6) and are listed in Figure 1-1.

Some organizations may find it inconvenient or even unnecessary to prepare a new project plan for each new set of analyses, especially analytical laboratories which receive numerous batches of samples from various customers within and outside their organizations. For these organizations, it is especially important that adequate QA management structures exist and that any procedures used exist as standard operating procedures (SOP), written documents which detail an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks. Having copies of SW-846 and all its referenced documents in one's laboratory is not a substitute for having in-house versions of the methods written to conform to specific instrumentation, data needs, and data quality requirements.

FIGURE 1-1

ESSENTIAL ELEMENTS OF A QA PROJECT PLAN

1. Title Page
2. Table of Contents
3. Project Description
4. Project Organization and Responsibility
5. QA Objectives
6. Sampling Procedures
7. Sample Custody
8. Calibration Procedures and Frequency
9. Analytical Procedures
10. Data Reduction, Validation, and Reporting
11. Internal Quality Control Checks
12. Performance and System Audits
13. Preventive Maintenance
14. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
15. Corrective Action
16. Quality Assurance Reports to Management

1.1.3 Organization and Responsibility

As part of any measurement program, activities for the data generators, data reviewers/approvers, and data users/requestors must be clearly defined. While the specific titles of these individuals will vary among agencies and laboratories, the most basic structure will include at least one representative of each of these three types. The data generator is typically the individual who carries out the analyses at the direction of the data user/requestor or a designate within or outside the laboratory. The data reviewer/approver is responsible for ensuring that the data produced by the data generator meet agreed-upon specifications.

Responsibility for data review is sometimes assigned to a "Quality Assurance Officer" or "QA Manager." This individual has broad authority to approve or disapprove project plans, specific analyses and final reports. The QA Officer is independent from the data generation activities. In general, the QA Officer is responsible for reviewing and advising on all aspects of QA/QC, including:

Assisting the data requestor in specifying the QA/QC procedure to be used during the program;

Making on-site evaluations and submitting audit samples to assist in reviewing QA/QC procedures; and,

If problems are detected, making recommendations to the data requestor and upper corporate/institutional management to ensure that appropriate corrective actions are taken.

In programs where large and complex amounts of data are generated from both field and laboratory activities, it is helpful to designate sampling monitors, analysis monitors, and quality control/data monitors to assist in carrying out the program or project.

The sampling monitor is responsible for field activities. These include:

Determining (with the analysis monitor) appropriate sampling equipment and sample containers to minimize contamination;

Ensuring that samples are collected, preserved, and transported as specified in the workplan; and

Checking that all sample documentation (labels, field notebooks, chain-of-custody records, packing lists) is correct and transmitting that information, along with the samples, to the analytical laboratory.

The analysis monitor is responsible for laboratory activities. These include:

Training and qualifying personnel in specified laboratory QC and analytical procedures, prior to receiving samples;

Receiving samples from the field and verifying that incoming samples correspond to the packing list or chain-of-custody sheet; and

Verifying that laboratory QC and analytical procedures are being followed as specified in the workplan, reviewing sample and QC data during the course of analyses, and, if questionable data exist, determining which repeat samples or analyses are needed.

The quality control and data monitor is responsible for QC activities and data management. These include:

Maintaining records of all incoming samples, tracking those samples through subsequent processing and analysis, and, ultimately, appropriately disposing of those samples at the conclusion of the program;

Preparing quality control samples for analysis prior to and during the program;

Preparing QC and sample data for review by the analysis coordinator and the program manager; and

Preparing QC and sample data for transmission and entry into a computer data base, if appropriate.

1.1.4 Performance and Systems Audits

The QA Officer may carry out performance and/or systems audits to ensure that data of known and defensible quality are produced during a program.

Systems audits are qualitative evaluations of all components of field and laboratory quality control measurement systems. They determine if the measurement systems are being used appropriately. The audits may be carried out before all systems are operational, during the program, or after the completion of the program. Such audits typically involve a comparison of the activities given in the QA/QC plan with those actually scheduled or performed. A special type of systems audit is the data management audit. This audit addresses only data collection and management activities.

The performance audit is a quantitative evaluation of the measurement systems of a program. It requires testing the measurement systems with samples of known composition or behavior to evaluate precision and accuracy. The performance audit is carried out by or under the auspices of the QA Officer without the knowledge of the analysts. Since this is seldom achievable, many variations are used that increase the awareness of the analyst as to the nature of the audit material.

1.1.5 Corrective Action

Corrective action procedures should be addressed in the program plan, project, or SOP. These should include the following elements:

The EPA predetermined limits for data acceptability beyond which corrective action is required;

Procedures for corrective action; and,

For each measurement system, identification of the individual responsible for initiating the corrective action and the individual responsible for approving the corrective action, if necessary.

The need for corrective action may be identified by system or performance audits or by standard QC procedures. The essential steps in the corrective action system are:

Identification and definition of the problem;

Assignment of responsibility for investigating the problem;

Investigation and determination of the cause of the problem;

Determination of a corrective action to eliminate the problem;

Assigning and accepting responsibility for implementing the corrective action;

Implementing the corrective action and evaluating its effectiveness; and

Verifying that the corrective action has eliminated the problem.

The QA Officer should ensure that these steps are taken and that the problem which led to the corrective action has been resolved.

1.1.6 QA/QC Reporting to Management

QA Project Program or Plans should provide a mechanism for periodic reporting to management (or to the data user) on the performance of the measurement system and the data quality. Minimally, these reports should include:

Periodic assessment of measurement quality indicators, i.e., data accuracy, precision and completeness;

Results of performance audits;

Results of system audits; and

Significant QA problems and recommended solutions.

The individual responsible within the organization structure for preparing the periodic reports should be identified in the organizational or management plan. The final report for each project should also include a separate QA section which summarizes data quality information contained in the periodic reports.

Other guidance on quality assurance management and organizations is available from the Agency and professional organizations such as ASTM, AOAC, APHA and FDA.

1.1.7 Quality Control Program for the Analysis of RCRA Samples

An analytical quality control program develops information which can be used to:

- Evaluate the accuracy and precision of analytical data in order to establish the quality of the data;
- Provide an indication of the need for corrections to the analytical system, when comparison with existing regulatory or program criteria or data trends shows that activities must be changed or monitored to a different degree; and
- To determine the effect of corrections to the analytical system.

1.1.8 Definitions

ACCURACY: Accuracy is the nearness of a measurement or the mean (\bar{x}) of a set of measurements to the true value. Accuracy is assessed by means of reference samples and percent recoveries.

ANALYTICAL BATCH: The basic unit for analytical quality control is the analytical batch. The analytical batch is defined as samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition (e.g. ground water, sludge, ash, etc.).

BLANKS:

CALIBRATION BLANK: Usually an organic or aqueous solution that is as free of analyte as possible and prepared with the same volume of chemical reagents used in the preparation of the calibration standards and diluted to the appropriate volume with the same solvent (water or organic) used in the preparation of the calibration standard. The calibration blank is used to give the null reading for the instrument response versus concentration calibration curve. One calibration blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

EQUIPMENT BLANK: Usually an organic or aqueous solution that is as free of analyte as possible and is transported to the site, opened in the field, and poured over or through the sample collection device, collected in a sample container, and returned to the laboratory. This serves as a check on

sampling device cleanliness. One equipment blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

FIELD BLANK: Usually an organic or aqueous solution that is as free of analyte as possible and is transferred from one vessel to another at the sampling site and preserved with the appropriate reagents. This serves as a check on reagent and environmental contamination. One field blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

REAGENT BLANK: Usually an organic or aqueous solution that is as free of analyte as possible and contains all the reagents in the same volume as used in the processing of the samples. The reagent blank must be carried through the complete sample preparation procedure and contains the same reagent concentrations in the final solution as in the sample solution used for analysis. The reagent blank is used to correct for possible contamination resulting from the preparation or processing of the sample. One reagent blank should be prepared for every analytical batch or for every 20 samples, whichever is greater.

TRIP BLANK: Usually an organic or aqueous solution that is as free of analyte as possible and is transported to the sampling site and returned to the laboratory without being opened. This serves as a check on sample contamination originating from sample transport, shipping, and from the site conditions. One trip blank should be analyzed with each analytical batch or every 20 samples, whichever is greater.

CHECK STANDARD: A material of known composition that is analyzed concurrently with test samples to evaluate a measurement process. An analytical standard that is analyzed to verify the calibration of the analytical system. One check standard should be analyzed with each analytical batch or every 20 samples, whichever is greater.

MATRIX SPIKE: A Matrix Spike is employed to provide a measure of accuracy for the method used in a given matrix. A matrix spike analysis is performed by adding a predetermined quantity of stock solutions of certain analytes to a sample matrix prior to sample extraction/digestion and analysis. The concentration of the spike should be at the regulatory standard level or the PQL for the method. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

MDL: The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration

is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

PRECISION: Precision is the agreement between a set of replicate measurements without assumption or knowledge of the true value. Precision is assessed by means of duplicate/replicate sample analysis.

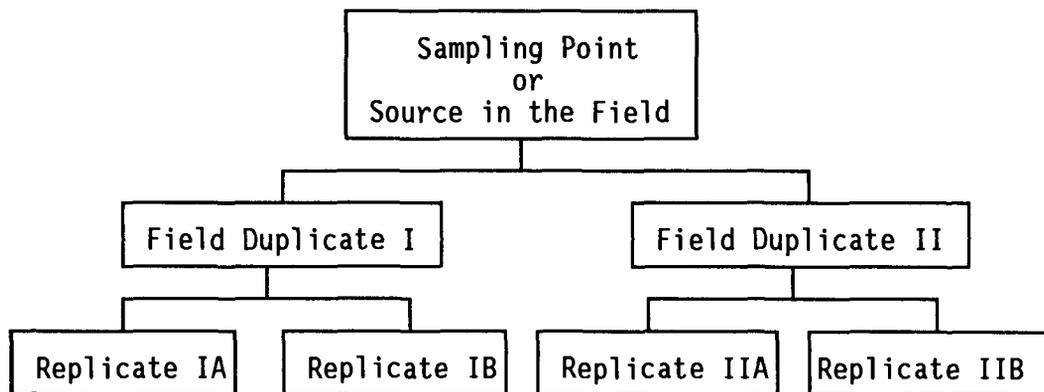
PQL: The practical quantitation limit (PQL) is the lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

RCRA: The Resource Conservation and Recovery Act.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

SAMPLES:

DUPLICATE SAMPLES: Duplicate samples are two separate samples taken from the same source (i.e. in separate containers and analyzed independently).



ENVIRONMENTAL SAMPLES:

An environmental sample or field sample is a representative sample of any material (aqueous, nonaqueous, or multimedia) collected from any source for which determination of composition or contamination is requested or required. For the purposes of this manual, environmental samples shall be classified as follows:
Surface Water and Ground Water;

Drinking Water -- delivered water (treated or untreated) designated as potable water;

Water/Wastewater -- raw source waters for public drinking water supplies, ground waters, municipal influents/effluents, and industrial influents/effluents;

Sludge -- municipal sludges and industrial sludges;

Waste -- aqueous and nonaqueous liquid wastes, chemical solids, contaminated soils, and industrial liquid and solid wastes.

QUALITY CONTROL REFERENCE SAMPLE: A sample prepared from an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analyte(s) of interest from a different source than that used in the preparation of standards for use in the standard curve. A quality control reference sample is intended as an independent check of technique, methodology, and standards and should be run with every analytical batch or every 20 samples, whichever is greater. This is applicable to all organic and inorganic analyses.

REPLICATE SAMPLES: Replicate samples are two aliquots taken from the same sample container and analyzed independently. In cases where aliquoting is impossible, as in the case of volatiles, duplicate samples must be taken for the replicate analysis.

STANDARD CURVE: A standard curve is a curve which plots concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by diluting the stock analyte solution in graduated amounts which cover the expected range of the samples being analyzed. Standards should be prepared at the frequency specified in the appropriate section. The calibration standards must be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: Surrogates are organic compounds which are similar to analytes of interest in chemical composition, extraction, and chromatography, but which are not normally found in environmental samples. These compounds are spiked into all blanks, calibration and check standards, samples (including duplicates and QC reference samples) and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

WATER: Any reference to water in a Chapter or Method refers to ASTM Type II reagent water (unless otherwise specified) which is free of contaminants that may interfere with the analytical test in question.

1.2 QUALITY CONTROL

The procedures indicated below are to be performed for all analyses. Specific instructions relevant to particular analyses are given in the pertinent analytical procedures.

1.2.1 Field Quality Control

The sampling component of the Quality Assurance Project Plan (QAPP) shall include as appropriate:

- Reference to or incorporation of accepted sampling techniques in the sampling plan;
- Procedures for documenting and justifying any field actions contrary to the accepted techniques;
- Documentation of all pre-field activities such as equipment check-out, calibrations, and container storage and preparation;
- Documentation of field measurement quality control data (quality control procedures for such measurements shall be equivalent to corresponding laboratory QC procedures);
- Documentation of field activities;
- Documentation of post-field activities including sample shipment and receipt, field team de-briefing and equipment check-in;
- Generation of quality control samples including field duplicate samples, field blanks, equipment blanks, and trip blanks; and
- The use of these samples in the context of data evaluation, with details of the methods employed (including statistical methods) and of the criteria upon which the information generated will be judged.

1.2.2 Analytical Quality Control

A quality control operation or component is only useful if it can be measured or documented. The following components of analytical quality control are related to the analytical batch. The procedures described are intended to be applied to chemical analytical procedures; although the principles are applicable to radio-chemical or biological analysis, the procedures may not be directly applicable to such techniques.

All quality control data and records required by these sections shall be retained by the laboratory for three years from the time the results were reported. The data must be made available to the client or enforcement official upon request.

1.2.2.1 Spikes, Blanks and Duplicates

General Requirements

These procedures shall be performed at least once with each analytical batch with a minimum of once per twenty samples.

1.2.2.1.1 Matrix Spiked Samples

A matrix spiked sample shall be analyzed with every analytical batch or every 20 samples, whichever is more frequent. The sample shall be spiked with the analyte(s) of interest (see the appropriate method). The sample to be spiked should be typical or representative of the batch. Ideally, it should be an intermediate between the cleanest and the most contaminated samples based on the best information available. It is recommended that the spike be made in a replicate of one of the field duplicate samples. This procedure is applicable to all organic or inorganic chemical analytes.

1.2.2.1.2 Field Duplicate Samples

Field duplicate samples shall be analyzed with every analytical batch or every 20 samples, whichever is greater. This procedure is applicable to all organic or inorganic chemical analytes.

1.2.2.1.3 Blanks

Each batch shall be accompanied by a reagent blank. The reagent blank shall be carried through the entire analytical procedure.

1.2.2.1.4 Surrogate Compounds

Every blank, standard, and environmental sample (including duplicates, QC reference samples, and check standards) shall be spiked with surrogate compounds prior to purging or extraction. Surrogates shall be spiked into samples according to the appropriate analytical methods. Surrogate spike recoveries shall fall within the control limits set by the laboratory (in accordance with procedures specified in the method or within $\pm 20\%$) for samples falling within the quantification limits without dilution. Dilution of samples to bring the analyte concentration into the linear range of calibration may dilute the surrogates below the quantification limit; evaluation of analytical quality then will rely on the quality control embodied in the check, spiked and duplicate spiked samples. This is applicable to organic analyses only.

1.2.2.1.5 Quality of Control Reference Sample

A quality control reference sample is a sample prepared from an independent standard at a concentration other than that used for calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes of interest from a different source than that used in the preparation of

standards for use in the standard curve. A quality control reference sample is intended as an independent check of technique, methodology, and standards and should be run with every analytical batch or every 20 samples, whichever is greater. This is applicable to all organic and inorganic analyses.

1.2.2.1.6 Check Standard

A standard of known concentration prepared by the analyst to monitor and verify instrument performance on a daily basis.

1.2.2.2 Clean-Ups

Quality control procedures described here are intended for adsorbent chromatography and back extractions applied to organic extracts. All batches of adsorbents (Florisol, alumina, silica gel, etc.) prepared for use shall be checked for analyte recovery by running the elution pattern with standards as a column check. The elution pattern shall be optimized for maximum recovery of analytes and maximum rejection of contaminants. This is applicable to organic analyses only.

1.2.2.2.1 Column Check Sample

The elution pattern shall be reconfirmed with a column check of standard compounds after activating or deactivating a batch of adsorbent. These compounds shall be representative of each elution fraction. Recovery as specified in the methods is considered an acceptable column check. A result lower than specified indicates that the procedure is not acceptable or has been misapplied. This is applicable to organic analyses only.

1.2.2.2.2 Column Check Blank

The column check blank shall be run after activating or deactivating a batch of adsorbent. This is applicable to organic analyses only.

1.2.2.3 Determinations

1.2.2.3.1 Instrument Adjustment, Tuning, and Alignment

Requirements and procedures are instrument- and method-specific. Analytical instrumentation shall be tuned and aligned in accordance with requirements which are specific to the instrumentation procedures employed. Individual determinative procedures shall be consulted. Criteria for initial conditions and for continuing confirmation conditions for methods within this manual are found in the appropriate procedures. This is applicable to all organic and inorganic analyses.

1.2.2.3.2 Calibration

Analytical instrumentation shall be calibrated in accordance with requirements which are specific to the instrumentation and procedures employed. Methods 6010, 7000, and 8000 as well as the appropriate analytical procedures shall be consulted for criteria for initial and continuing calibration.

1.2.2.3.3 Additional QC Requirements for Inorganic Analysis

Standard curves used in the determination of inorganic analytes shall be prepared as follows:

Standard curves derived from data consisting of one calibration blank and three concentrations shall be prepared for each analyte. The response for each prepared standard shall be based upon the average of three replicate readings of each standard. The standard curve shall be used with each subsequent analysis provided that the standard curve is verified by using at least one reagent blank and one standard at a level normally encountered or expected in such samples. The response for each standard shall be based upon the average of three replicate readings of the standard. If the results of the verification are not within $\pm 10\%$ of the original curve, a new standard shall be prepared and analyzed. If the results of the second verification are not within $\pm 10\%$ of the original standard curve, a reference standard should be employed to determine if the discrepancy is with the standard or with the instrument. New standards should also be prepared on a quarterly basis at a minimum. All data used in drawing or describing the curve shall be so indicated on the curve or its description. A record shall be made of the verification.

Standard deviations and relative standard deviations shall be calculated for the percent recovery of analytes from the spiked sample duplicates and from the check samples. These values shall be established for the twenty most recent determinations in each category.

1.2.2.3.4 Additional Quality Control Requirements for Organic Analysis

The following requirements shall be applied to the analysis of samples by gas chromatography, liquid chromatography and gas chromatography/mass spectrometry.

The calibration of each instrument shall be verified at frequencies specified in the methods. A new standard curve must be prepared as specified in the methods.

The tune of each GC/MS system used for the determination of organic analytes shall be checked with 4-bromofluorobenzene (BFB) for determinations of volatiles and with decafluorotriphenylphosphine (DFTPP) for determinations of semi-volatiles. The required ion

abundance criteria shall be met before determination of any analytes. If the system does not meet the required specification for one or more of the required ions, the instrument must be retuned and rechecked before proceeding with sample analysis. The tune performance check criteria must be achieved daily or for each 12 hour operating period, whichever is more frequent.

Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. Background subtraction actions resulting in spectral distortions for the sole purpose of meeting special requirements are contrary to the objectives of Quality Assurance and are unacceptable.

For determinations by HPLC or GC, the instrument calibration shall be verified as specified in the methods.

1.2.2.3.5 Identification

Identification of all analytes must be accomplished with an authentic standard of the analyte. When authentic standards are not available, identification is tentative.

For gas chromatographic determinations of specific analytes, the relative retention time of the unknown must be compared with that of an authentic standard. For compound confirmation, a sample and standard shall be re-analyzed on a column of different selectivity to obtain a second characteristic relative retention time. Peaks must elute within daily retention time windows to be declared a tentative or confirmed identification.

For gas chromatographic/mass spectrometric determinations of specific analytes, the spectrum of the analyte should conform to a literature representation of the spectrum or to a spectrum of the authentic standard obtained after satisfactory tuning of the mass spectrometer and within the same twelve-hour working shift as the analytical spectrum. The appropriate analytical methods should be consulted for specific criteria for matching the mass spectra, relative response factors, and relative retention times to those of authentic standards.

1.2.2.3.6 Quantification

The procedures for quantification of analytes are discussed in the appropriate general procedures (7000, 8000) and the specific analytical methods.

In some situations in the course of determining metal analytes, matrix-matched calibration standards may be required. These standards shall be composed of the pure reagent, approximation of the matrix, and reagent addition of major interferences in the samples. This will be stipulated in the procedures.

Estimation of the concentration of an organic compound not contained within the calibration standard may be accomplished by comparing mass spectral response of the compound with that of an internal standard. The procedure is specified in the methods.

1.3 METHOD DETECTION LIMIT

For operational purposes, when it is necessary to determine the method detection limit in the sample matrix, the MDL defined in One-10 shall be determined by multiplying by 7 the standard deviation obtained from the triplicate analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL.

- Determine the estimated MDL as follows:

Obtain the concentration value that corresponds to:

- a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or
- b) the region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.

- Determine the variance (S^2) for each analyte as follows:

$$S^2 = 1/(n - 1) \left[\sum_{i=1}^n X_i^2 - 1/n \left(\sum_{i=1}^n X_i \right)^2 \right]$$

- Determine the standard deviation (S) for each analyte as follows:

$$S = (S^2)^{1/2}$$

- Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1, 1-\alpha = 0.99)} (S)$$

where $t_{(n-1, 1-\alpha = 0.99)} = 6.965$ for three replicates as determined from the table of student's t values at the 99 percent level.

1.4 DATA REPORTING

The requirement of reporting analytical results on a wet-weight or a dry-weight basis is dictated by factors such as: sample matrix; program or regulatory requirement; and objectives of the analysis.

Analytical results shall be reported with the percent moisture or percent solid content of the sample.

1.5 QUALITY CONTROL DOCUMENTATION

The following sections list the QC documentation which comprises the complete analytical package. This package can be obtained from the data generator upon request. These forms, or adaptations of these forms, shall be

used by the data generator/reportor for inorganics (I), or for organics (O) or both (I/O) types of determinations.

1.5.1 Analytical Results (I/O: Form I)

Analyte concentration.

Sample weight.

Percent water (for non-aqueous samples when specified).

Final volume of extract or diluted sample.

Holding times (I: Form X).

1.5.2 Calibration (I: Form 2A; O: Form V, VI, VII, IX)

Calibration curve or coefficients of the linear equation which describes the calibration curve.

Correlation coefficient of the linear calibration.

Concentration/response data (or relative response data) of the calibration check standards, along with dates on which they were analytically determined.

1.5.3 Column Check (O: Form X)

Results of column chromatography check, with the chromatogram.

1.5.4 Extraction/Digestion (I/O: Form I)

Date of the extraction for each sample.

1.5.5 Surrogates (O: Form II)

Amount of surrogate spiked, and percent recovery of each surrogate.

1.5.6 Matrix Spiked Samples (I: Form 5, 5A, 6; O: Form III)

Amount spiked, percent recovery, and relative percent difference for each compound in the spiked samples for the analytical batch.

1.5.7 Check Standard (I: Form 7; O: Form VIII)

Amount spiked, and percent recovery of each compound spiked.

1.5.8 Blank (I: Form 3; O: Form IV)

Identity and amount of each constituent.

1.5.9 Chromatograms (for organic analysis)

All chromatograms for reported results, properly labeled with:

- Sample identification
- Method identification
- Identification of retention time of analyte on the chromatograms.

1.5.10 Quantitative Chromatogram Report (0: Forms VIII, IX, X)

Retention time of analyte.
Amount injected.
Area of appropriate calculation of detection response.
Amount of analyte found.
Date and time of injection.

1.5.11 Mass Spectrum

Spectra of standards generated from authentic standards (one for each report for each compound detected).

Spectra of analytes from actual analyses.

Spectrometer identifier.

1.5.12 Metal Interference Check Sample Results (I: Form 4)

1.5.13 Detection Limit (I: Form 7; 0: Form I)

Analyte detection limits with methods of estimation.

1.5.14 Results of Standard Additions (I: Form 8)

1.5.15 Results of Serial Dilutions (I: Form 9)

1.5.16 Instrument Detection Limits (I: Form 11)

1.5.17 ICP Interelement Correction Factors and ICP Linear Ranges (when applicable) (I: Form 12a, 12b, Form 13).

1.6 REFERENCES

1. Guidelines and Specifications for Preparing Quality Assurance Program Plans, September 20, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-004/80, Washington, DC 20460.
2. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans, December 29, 1980, Office of Monitoring Systems and Quality Assurance, ORD, U.S. EPA, QAMS-005/80, Washington, DC 20460.

1
INORGANIC ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Lab Sample ID: _____

Level (low/med): _____ Date Received: _____

% Solids: _____

Concentration Units (ug/L or mg/kg dry weight): _____

CAS No.	Analyte	Concentration	C	M	Q
7429-90-5	Aluminum				
7440-36-0	Antimony				
7440-38-2	Arsenic				
7440-39-3	Barium				
7440-41-7	Beryllium				
7440-43-9	Cadmium				
7440-70-2	Calcium				
7440-47-3	Chromium				
7440-48-4	Cobalt				
7440-50-8	Copper				
7439-89-6	Iron				
7439-92-1	Lead				
7439-95-4	Magnesium				
7439-96-5	Manganese				
7439-97-6	Mercury				
7440-02-0	Nickel				
7440-09-7	Potassium				
7782-49-2	Selenium				
7440-22-4	Silver				
7440-23-5	Sodium				
7440-28-0	Thallium				
7440-62-2	Vanadium				
7440-66-6	Zinc				
	Cyanide				

Color Before: _____ Clarity Before: _____ Texture: _____

Color After: _____ Clarity After: _____ Artifacts: _____

Comments:

2A
 INITIAL AND CONTINUING CALIBRATION VERIFICATION

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Initial Calibration Source: _____
 Continuing Calibration Source: _____

Concentration Units: ug/L

Analyte	Initial Calibration			Continuing Calibration					M
	True	Found	%R(1)	True	Found	%R(1)	Found	%R(1)	
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

(1) Control Limits: Mercury 80-120; Other Metals 90-110; Cyanide 85-115

2B
CRDL STANDARD FOR AA AND ICP

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 AA CRDL Standard Source: _____
 ICP CRDL Standard Source: _____

Concentration Units: ug/L

Analyte	CRDL Standard for AA			CRDL Standard for ICP				
	True	Found	%R	True	Initial Found	%R	Final Found	%R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

3
BLANKS

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Preparation Blank Matrix (soil/water): _____
 Preparation Blank Concentration Units (ug/L or mg/kg): _____

Analyte	Initial Calib. Blank (ug/L)	C	Continuing Calibration Blank (ug/L)						Prepa- ration Blank	C	M
			1	C	2	C	3	C			
Aluminum											
Antimony											
Arsenic											
Barium											
Beryllium											
Cadmium											
Calcium											
Chromium											
Cobalt											
Copper											
Iron											
Lead											
Magnesium											
Manganese											
Mercury											
Nickel											
Potassium											
Selenium											
Silver											
Sodium											
Thallium											
Vanadium											
Zinc											
Cyanide											

ICP INTERFERENCE CHECK SAMPLE

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ ICS Source: _____

Concentration Units: ug/L

Analyte	True		Initial Found			Final Found		
	Sol. A	Sol. AB	Sol. A	Sol. AB	%R	Sol. A	Sol. AB	%R
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								

5A
SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit %R	Spiked Sample Result (SSR) C	Sample Result (SR) C	Spike Added (SA)	%R	Q	M
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							
Cyanide							

Comments:

5B
POST DIGEST SPIKE SAMPLE RECOVERY

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units: ug/L

Analyte	Control Limit %R	Spiked Sample Result (SSR)	C	Sample Result (SR)	C	Spike Added (SA)	%R	Q	M
Aluminum									
Antimony									
Arsenic									
Barium									
Beryllium									
Cadmium									
Calcium									
Chromium									
Cobalt									
Copper									
Iron									
Lead									
Magnesium									
Manganese									
Mercury									
Nickel									
Potassium									
Selenium									
Silver									
Sodium									
Thallium									
Vanadium									
Zinc									
Cyanide									

Comments:

6
DUPLICATES

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

% Solids for Sample: _____ % Solids for Duplicate: _____

Concentration Units (ug/L or mg/kg dry weight): _____

Analyte	Control Limit	Sample (S)	C	Duplicate (D)	C	RPD	Q	M
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								

7
LABORATORY CONTROL SAMPLE

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Solid LCS Source: _____
 Aqueous LCS Source: _____

Analyte	Aqueous (ug/L)			Solid (mg/kg)				%R
	True	Found	%R	True	Found	C	Limits	
Aluminum								
Antimony								
Arsenic								
Barium								
Beryllium								
Cadmium								
Calcium								
Chromium								
Cobalt								
Copper								
Iron								
Lead								
Magnesium								
Manganese								
Mercury								
Nickel								
Potassium								
Selenium								
Silver								
Sodium								
Thallium								
Vanadium								
Zinc								
Cyanide								

9
ICP SERIAL DILUTIONS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix (soil/water): _____ Level (low/med): _____

Concentration Units: ug/L

Analyte	Initial Sample		Serial Dilution		% Difference	Q	M
	Result (I)	C	Result (S)	C			
Aluminum							
Antimony							
Arsenic							
Barium							
Beryllium							
Cadmium							
Calcium							
Chromium							
Cobalt							
Copper							
Iron							
Lead							
Magnesium							
Manganese							
Mercury							
Nickel							
Potassium							
Selenium							
Silver							
Sodium							
Thallium							
Vanadium							
Zinc							

INSTRUMENT DETECTION LIMITS (QUARTERLY)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____
 Flame AA ID Number: _____
 Furnace AA ID Number: _____

Analyte	Wave-length (nm)	Back-ground	CRDL (ug/L)	IDL (ug/L)	M
Aluminum			200		
Antimony			60		
Arsenic			10		
Barium			200		
Beryllium			5		
Cadmium			5		
Calcium			5000		
Chromium			10		
Cobalt			50		
Copper			25		
Iron			100		
Lead			5		
Magnesium			5000		
Manganese			15		
Mercury			0.2		
Nickel			40		
Potassium			5000		
Selenium			5		
Silver			10		
Sodium			5000		
Thallium			10		
Vanadium			50		
Zinc			20		

Comments:

12A
ICP INTERELEMENT CORRECTION FACTORS (QUARTERLY)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for:				
		Al	Ca	Fe	Mg	—
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

12B
ICP INTERELEMENT CORRECTION FACTORS (QUARTERLY)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Wave-length (nm)	Interelement Correction Factors for:				
		—	—	—	—	—
Aluminum						
Antimony						
Arsenic						
Barium						
Beryllium						
Cadmium						
Calcium						
Chromium						
Cobalt						
Copper						
Iron						
Lead						
Magnesium						
Manganese						
Mercury						
Nickel						
Potassium						
Selenium						
Silver						
Sodium						
Thallium						
Vanadium						
Zinc						

Comments:

13
ICP LINEAR RANGES (QUARTERLY)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 ICP ID Number: _____ Date: _____

Analyte	Integ. Time (Sec.)	Concentration (ug/L)	M
Aluminum			
Antimony			
Arsenic			
Barium			
Beryllium			
Cadmium			
Calcium			
Chromium			
Cobalt			
Copper			
Iron			
Lead			
Magnesium			
Manganese			
Mercury			
Nickel			
Potassium			
Selenium			
Silver			
Sodium			
Thallium			
Vanadium			
Zinc			

Comments:

1A
VOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____ (g/mL) _____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec. _____ Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

CONCENTRATION UNITS:
(ug/L or ug/Kg) _____ Q

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) _____	Q
74-87-3	-----Chloromethane		
74-83-9	-----Bromomethane		
75-01-4	-----Vinyl Chloride		
75-00-3	-----Chloroethane		
75-09-2	-----Methylene Chloride		
67-64-1	-----Acetone		
75-15-0	-----Carbon Disulfide		
75-35-4	-----1,1-Dichloroethene		
75-34-3	-----1,1-Dichloroethane		
540-59-0	-----1,2-Dichloroethene (total)		
67-66-3	-----Chloroform		
107-06-2	-----1,2-Dichloroethane		
78-93-3	-----2-Butanone		
71-55-6	-----1,1,1-Trichloroethane		
56-23-5	-----Carbon Tetrachloride		
108-05-4	-----Vinyl Acetate		
75-27-4	-----Bromodichloromethane		
78-87-5	-----1,2-Dichloropropane		
10061-01-5	-----cis-1,3-Dichloropropene		
79-01-6	-----Trichloroethene		
124-48-1	-----Dibromochloromethane		
79-00-5	-----1,1,2-Trichloroethane		
71-43-2	-----Benzene		
10061-02-6	-----trans-1,3-Dichloropropene		
75-25-2	-----Bromoform		
108-10-1	-----4-Methyl-2-Pentanone		
591-78-6	-----2-Hexanone		
127-18-4	-----Tetrachloroethene		
79-34-5	-----1,1,2,2-Tetrachloroethane		
108-88-3	-----Toluene		
108-90-7	-----Chlorobenzene		
100-41-4	-----Ethylbenzene		
100-42-5	-----Styrene		
1330-20-7	-----Xylene (total)		

1B
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____ (g/mL) _____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec. _____ dec. _____ Date Extracted: _____

Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____

GPC Cleanup: (Y/N) _____ pH: _____ Dilution Factor: _____

CONCENTRATION UNITS:

CAS NO. COMPOUND (ug/L or ug/Kg) _____ Q

108-95-2-----	Phenol		
111-44-4-----	bis(2-Chloroethyl) ether		
95-57-8-----	2-Chlorophenol		
541-73-1-----	1,3-Dichlorobenzene		
106-46-7-----	1,4-Dichlorobenzene		
100-51-6-----	Benzyl alcohol		
95-50-1-----	1,2-Dichlorobenzene		
95-48-7-----	2-Methylphenol		
108-60-1-----	bis(2-Chloroisopropyl) ether		
106-44-5-----	4-Methylphenol		
621-64-7-----	N-Nitroso-di-n-propylamine		
67-72-1-----	Hexachloroethane		
98-95-3-----	Nitrobenzene		
78-59-1-----	Isophorone		
88-75-5-----	2-Nitrophenol		
105-67-9-----	2,4-Dimethylphenol		
65-85-0-----	Benzoic acid		
111-91-1-----	bis(2-Chloroethoxy)methane		
120-83-2-----	2,4-Dichlorophenol		
120-82-1-----	1,2,4-Trichlorobenzene		
91-20-3-----	Naphthalene		
106-47-8-----	4-Chloroaniline		
87-68-3-----	Hexachlorobutadiene		
59-50-7-----	4-Chloro-3-methylphenol		
91-57-6-----	2-Methylnaphthalene		
77-47-4-----	Hexachlorocyclopentadiene		
88-06-2-----	2,4,6-Trichlorophenol		
95-95-4-----	2,4,5-Trichlorophenol		
91-58-7-----	2-Chloronaphthalene		
88-74-4-----	2-Nitroaniline		
131-11-3-----	Dimethylphthalate		
208-96-8-----	Acenaphthylene		
606-20-2-----	2,6-Dinitrotoluene		

1D
PESTICIDE ORGANICS ANALYSIS DATA SHEET

EPA SAMPLE NO.

- - -

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Matrix: (soil/water) _____ Lab Sample ID: _____
 Sample wt/vol: _____ (g/mL) _____ Lab File ID: _____
 Level: (low/med) _____ Date Received: _____
 % Moisture: not dec. _____ dec. _____ Date Extracted: _____
 Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____
 GPC Cleanup: (Y/N) _____ pH: _____ Dilution Factor: _____

CONCENTRATION UNITS:
(ug/L or ug/Kg) _____ Q

CAS NO.	COMPOUND	CONCENTRATION UNITS: (ug/L or ug/Kg) _____	Q
319-84-6	alpha-BHC		
319-85-7	beta-BHC		
319-86-8	delta-BHC		
58-89-9	gamma-BHC (Lindane)		
76-44-8	Heptachlor		
309-00-2	Aldrin		
1024-57-3	Heptachlor epoxide		
959-98-8	Endosulfan I		
60-57-1	Dieldrin		
72-55-9	4,4'-DDE		
72-20-8	Endrin		
33213-65-9	Endosulfan II		
72-54-8	4,4'-DDD		
1031-07-8	Endosulfan sulfate		
50-29-3	4,4'-DDT		
72-43-5	Methoxychlor		
53494-70-5	Endrin ketone		
5103-71-9	alpha-Chlordane		
5103-74-2	gamma-Chlordane		
8001-35-2	Toxaphene		
12674-11-2	Aroclor-1016		
11104-28-2	Aroclor-1221		
11141-16-5	Aroclor-1232		
53469-21-9	Aroclor-1242		
12672-29-6	Aroclor-1248		
11097-69-1	Aroclor-1254		
11096-82-5	Aroclor-1260		

1E
VOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____ (g/mL) _____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec. _____ Date Analyzed: _____

Column: (pack/cap) _____ Dilution Factor: _____

CONCENTRATION UNITS:
(ug/L or ug/Kg) _____

Number TICs found: _____

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

1F
SEMIVOLATILE ORGANICS ANALYSIS DATA SHEET
TENTATIVELY IDENTIFIED COMPOUNDS

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix: (soil/water) _____ Lab Sample ID: _____

Sample wt/vol: _____ (g/mL) _____ Lab File ID: _____

Level: (low/med) _____ Date Received: _____

% Moisture: not dec. _____ dec. _____ Date Extracted: _____

Extraction: (SepF/Cont/Sonc) _____ Date Analyzed: _____

GPC Cleanup: (Y/N) _____ pH: _____ Dilution Factor: _____

Number TICs found: _____ CONCENTRATION UNITS:
 (ug/L or ug/Kg) _____

CAS NUMBER	COMPOUND NAME	RT	EST. CONC.	Q
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				
9.				
10.				
11.				
12.				
13.				
14.				
15.				
16.				
17.				
18.				
19.				
20.				
21.				
22.				
23.				
24.				
25.				
26.				
27.				
28.				
29.				
30.				

2B
SOIL VOLATILE SURROGATE RECOVERY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Level: (low/med) _____

	EPA SAMPLE NO.	S1 (TOL) #	S2 (BFB) #	S3 (DCE) #	OTHER	TOT OUT
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						

QC LIMITS

S1 (TOL) = Toluene-d8 (81-117)
 S2 (BFB) = Bromofluorobenzene (74-121)
 S3 (DCE) = 1,2-Dichloroethane-d4 (70-121)

Column to be used to flag recovery values

* Values outside of contract required QC limits

D Surrogates diluted out

2D
SOIL SEMIVOLATILE SURROGATE RECOVERY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Level: (low/med) _____

	EPA SAMPLE NO.	S1 (NBZ) #	S2 (FBP) #	S3 (TPH) #	S4 (PHL) #	S5 (2FP) #	S6 (TBP) #	OTHER	TOT OUT
01									
02									
03									
04									
05									
06									
07									
08									
09									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

QC LIMITS

S1 (NBZ) = Nitrobenzene-d5 (23-120)
 S2 (FBP) = 2-Fluorobiphenyl (30-115)
 S3 (TPH) = Terphenyl-d14 (18-137)
 S4 (PHL) = Phenol-d6 (24-113)
 S5 (2FP) = 2-Fluorophenol (25-121)
 S6 (TBP) = 2,4,6-Tribromophenol (19-122)

Column to be used to flag recovery values
 * Values outside of contract required QC limits
 D Surrogates diluted out

2F
SOIL PESTICIDE SURROGATE RECOVERY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Level: (low/med) _____

	EPA SAMPLE NO.	S1 (DBC) #	OTHER
01			
02			
03			
04			
05			
06			
07			
08			
09			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
21			
22			
23			
24			
25			
26			
27			
28			
29			
30			

ADVISORY
QC LIMITS
(24-150)

S1 (DBC) = Dibutylchlorendate

Column to be used to flag recovery values

* Values outside of QC limits

D Surrogates diluted out

SOIL VOLATILE MATRIX SPIKE/MATRIX SPIKE' DUPLICATE RECOVERY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Matrix Spike - EPA Sample No.: _____ Level: (low/med) _____

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	MS CONCENTRATION (ug/Kg)	MS % REC #	QC LIMITS REC.
1,1-Dichloroethene					59-172
Trichloroethene					62-137
Benzene					66-142
Toluene					59-139
Chlorobenzene					60-133

COMPOUND	SPIKE ADDED (ug/Kg)	MSD CONCENTRATION (ug/Kg)	MSD % REC #	% RPD #	QC LIMITS RPD	REC.
1,1-Dichloroethene					22	59-172
Trichloroethene					24	62-137
Benzene					21	66-142
Toluene					21	59-139
Chlorobenzene					21	60-133

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD: _____ out of _____ outside limits

Spike Recovery: _____ out of _____ outside limits

COMMENTS: _____

3D
SOIL SEMIVOLATILE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Matrix Spike - EPA Sample No.: _____ Level: (low/med) _____

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	MS CONCENTRATION (ug/Kg)	MS % REC #	QC LIMITS REC.
Phenol					26- 90
2-Chlorophenol					25-102
1,4-Dichlorobenzene					28-104
N-Nitroso-di-n-prop. (1)					41-126
1,2,4-Trichlorobenzene					38-107
4-Chloro-3-methylphenol					26-103
Acenaphthene					31-137
4-Nitrophenol					11-114
2,4-Dinitrotoluene					28- 89
Pentachlorophenol					17-109
Pyrene					35-142

COMPOUND	SPIKE ADDED (ug/Kg)	MSD CONCENTRATION (ug/Kg)	MSD % REC #	% RPD #	QC LIMITS RPD REC.
Phenol					35 26- 90
2-Chlorophenol					50 25-102
1,4-Dichlorobenzene					27 28-104
N-Nitroso-di-n-prop. (1)					38 41-126
1,2,4-Trichlorobenzene					23 38-107
4-Chloro-3-methylphenol					33 26-103
Acenaphthene					19 31-137
4-Nitrophenol					50 11-114
2,4-Dinitrotoluene					47 28- 89
Pentachlorophenol					47 17-109
Pyrene					36 35-142

(1) N-Nitroso-di-n-propylamine

Column to be used to flag recovery and RPD values with an asterisk
 * Values outside of QC limits

RPD: _____ out of _____ outside limits
 Spike Recovery: _____ out of _____ outside limits

COMMENTS: _____

3F
SOIL PESTICIDE MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Matrix Spike - EPA Sample No.: _____ Level: (low/med) _____

COMPOUND	SPIKE ADDED (ug/Kg)	SAMPLE CONCENTRATION (ug/Kg)	MS CONCENTRATION (ug/Kg)	MS % REC #	QC. LIMITS REC.
gamma-BHC (Lindane)					46-127
Heptachlor					35-130
Aldrin					34-132
Dieldrin					31-134
Endrin					42-139
4,4'-DDT					23-134

COMPOUND	SPIKE ADDED (ug/Kg)	MSD CONCENTRATION (ug/Kg)	MSD % REC #	% RPD #	QC LIMITS RPD	REC.
gamma-BHC (Lindane)					50	46-127
Heptachlor					31	35-130
Aldrin					43	34-132
Dieldrin					38	31-134
Endrin					45	42-139
4,4'-DDT					50	23-134

Column to be used to flag recovery and RPD values with an asterisk

* Values outside of QC limits

RPD: _____ out of _____ outside limits
 Spike Recovery: _____ out of _____ outside limits

COMMENTS: _____

4A
VOLATILE METHOD BLANK SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID: _____ Lab Sample ID: _____
 Date Analyzed: _____ Time Analyzed: _____
 Matrix: (soil/water) _____ Level: (low/med) _____
 Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	TIME ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

4B
SEMIVOLATILE METHOD BLANK SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID: _____ Lab Sample ID: _____
 Date Extracted: _____ Extraction: (SepF/Cont/Sonc) _____
 Date Analyzed: _____ Time Analyzed: _____
 Matrix: (soil/water) _____ Level: (low/med) _____
 Instrument ID: _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				
27				
28				
29				
30				

COMMENTS: _____

4C
PESTICIDE METHOD BLANK SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab Sample ID: _____ Lab File ID: _____
 Matrix: (soil/water) _____ Level: (low/med) _____
 Date Extracted: _____ Extraction: (SepF/Cont/Sonc) _____
 Date Analyzed (1): _____ Date Analyzed (2): _____
 Time Analyzed (1): _____ Time Analyzed (2): _____
 Instrument ID (2): _____ Instrument ID (2): _____
 GC Column ID (1): _____ GC Column ID (1): _____

THIS METHOD BLANK APPLIES TO THE FOLLOWING SAMPLES, MS AND MSD:

	EPA SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED 1	DATE ANALYZED 2
01				
02				
03				
04				
05				
06				
07				
08				
09				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				
26				

COMMENTS: _____

5A
VOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - BROMOFLUOROBENZENE (BFB)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID: _____ BFB Injection Date: _____
 Instrument ID: _____ BFB Injection Time: _____
 Matrix: (soil/water) _____ Level: (low/med) _____ Column: (pack/cap) _____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
50	15.0 - 40.0% of mass 95	
75	30.0 - 60.0% of mass 95	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of mass 95	
173	Less than 2.0% of mass 174	() 1
174	Greater than 50.0% of mass 95	
175	5.0 - 9.0% of mass 174	() 1
176	Greater than 95.0%, but less than 101.0% of mass 174	() 1
177	5.0 - 9.0% of mass 176	() 2

1-Value is % mass 174

2-Value is % mass 176

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

5B
SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS
CALIBRATION - DECAFLUOROTRIPHENYLPHOSPHINE (DFTPP)

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID: _____ DFTPP Injection Date: _____
 Instrument ID: _____ DFTPP Injection Time: _____

m/e	ION ABUNDANCE CRITERIA	% RELATIVE ABUNDANCE
51	30.0 - 60.0% of mass 198	
68	Less than 2.0% of mass 69	() 1
69	Mass 69 relative abundance	
70	Less than 2.0% of mass 69	() 1
127	40.0 - 60.0% of mass 198	
197	Less than 1.0% of mass 198	
198	Base Peak, 100% relative abundance	
199	5.0 to 9.0% of mass 198	
275	10.0 - 30.0% of mass 198	
365	Greater than 1.00% of mass 198	
441	Present, but less than mass 443	
442	Greater than 40.0% of mass 198	
443	17.0 - 23.0% of mass 442	() 2

1-Value is % mass 69

2-Value is % mass 442

THIS TUNE APPLIES TO THE FOLLOWING SAMPLES, MS, MSD, BLANKS, AND STANDARDS:

	EPA SAMPLE NO.	LAB SAMPLE ID	LAB FILE ID	DATE ANALYZED	TIME ANALYZED
01					
02					
03					
04					
05					
06					
07					
08					
09					
10					
11					
12					
13					
14					
15					
16					
17					
18					
19					
20					
21					
22					

page ___ of ___

6A
VOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Instrument ID: _____ Calibration Date(s): _____
 Matrix: (soil/water) _____ Level: (low/med) _____ Column: (pack/cap) _____
 Min RRF for SPCC(#) = 0.300 (0.250 for Bromoform) Max %RSD for CCC(*) = 30.0%

LAB FILE ID: _____ RRF20 = _____ RRF50 = _____
 RRF100 = _____ RRF150 = _____ RRF200 = _____

COMPOUND	RRF20	RRF50	RRF100	RRF150	RRF200	RRF	% RSD
Chloromethane	#						#
Bromomethane							
Vinyl Chloride	*						*
Chloroethane							
Methylene Chloride							
Acetone							
Carbon Disulfide							
1,1-Dichloroethene	*						*
1,1-Dichloroethane	#						#
1,2-Dichloroethene (total)							
Chloroform	*						*
1,2-Dichloroethane							
2-Butanone							
1,1,1-Trichloroethane							
Carbon Tetrachloride							
Vinyl Acetate							
Bromodichloromethane							
1,2-Dichloropropane	*						*
cis-1,3-Dichloropropene							
Trichloroethene							
Dibromochloromethane							
1,1,2-Trichloroethane							
Benzene							
trans-1,3-Dichloropropene							
Bromoform	#						#
4-Methyl-2-Pentanone							
2-Hexanone							
Tetrachloroethene							
1,1,2,2-Tetrachloroethane	#						#
Toluene	*						*
Chlorobenzene	#						#
Ethylbenzene	*						*
Styrene							
Xylene (total)							
Toluene-d8							
Bromofluorobenzene							
1,2-Dichloroethane-d4							

SEMIVOLATILE ORGANICS INITIAL CALIBRATION DATA

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ Calibration Date(s): _____

Min \overline{RRF} for SPCC(#) = 0.050

Max %RSD for CCC(*) = 30.0%

LAB FILE ID:		RRF20 = _____	RRF50 = _____				
RRF80 = _____		RRF120 = _____	RRF160 = _____				
COMPOUND	RRF20	RRF50	RRF80	RRF120	RRF160	\overline{RRF}	% RSD
Phenol	*						*
bis(2-Chloroethyl)ether							
2-Chlorophenol							
1,3-Dichlorobenzene							
1,4-Dichlorobenzene	*						*
Benzyl alcohol							
1,2-Dichlorobenzene							
2-Methylphenol							
bis(2-Chloroisopropyl) ether							
4-Methylphenol							
N-Nitroso-di-n-propylamine	#						#
Hexachloroethane							
Nitrobenzene							
Isophorone							
2-Nitrophenol	*						*
2,4-Dimethylphenol							
Benzoic acid							
bis(2-Chloroethoxy)methane							
2,4-Dichlorophenol	*						*
1,2,4-Trichlorobenzene							
Naphthalene							
4-Chloroaniline							
Hexachlorobutadiene	*						*
4-Chloro-3-methylphenol	*						*
2-Methylnaphthalene							
Hexachlorocyclopentadiene	#						#
2,4,6-Trichlorophenol	*						*
2,4,5-Trichlorophenol							
2-Chloronaphthalene							
2-Nitroaniline							
Dimethylphthalate							
Acenaphthylene							
2,6-Dinitrotoluene							
3-Nitroaniline							
Acenaphthene	*						*
2,4-Dinitrophenol	#						#
4-Nitrophenol	#						#

7A
VOLATILE CONTINUING CALIBRATION CHECK

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Instrument ID: _____ Calibration Date: _____ Time: _____
 Lab File ID: _____ Init. Calib. Date(s): _____
 Matrix: (soil/water) _____ Level: (low/med) _____ Column: (pack/cap) _____
 Min RRF50 for SPCC(#) = 0.300 (0.250 for Bromoform) Max %D for CCC(*) = 25.0%

COMPOUND	RRF	RRF50	%D
Chloromethane	#		#
Bromomethane			
Vinyl Chloride	*		*
Chloroethane			
Methylene Chloride			
Acetone			
Carbon Disulfide			
1,1-Dichloroethene	*		*
1,1-Dichloroethane	#		#
1,2-Dichloroethene (total)			
Chloroform	*		*
1,2-Dichloroethane			
2-Butanone			
1,1,1-Trichloroethane			
Carbon Tetrachloride			
Vinyl Acetate			
Bromodichloromethane			
1,2-Dichloropropane	*		*
cis-1,3-Dichloropropene			
Trichloroethene			
Dibromochloromethane			
1,1,2-Trichloroethane			
Benzene			
trans-1,3-Dichloropropene			
Bromoform	#		#
4-Methyl-2-Pentanone			
2-Hexanone			
Tetrachloroethene			
1,1,2,2-Tetrachloroethane	#		#
Toluene	*		*
Chlorobenzene	#		#
Ethylbenzene	*		*
Styrene			
Xylene (total)			
Toluene-d8			
Bromofluorobenzene			
1,2-Dichloroethane-d4			

8A
VOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID (Standard): _____ Date Analyzed: _____
 Instrument ID: _____ Time Analyzed: _____
 Matrix: (soil/water) _____ Level: (low/med) _____ Column: (pack/cap) _____

	IS1 (BCM)	RT	IS2 (DFB)	RT	IS3 (CBZ)	RT
	AREA #		AREA #		AREA #	
=====	=====	=====	=====	=====	=====	=====
12 HOUR STD						
=====	=====	=====	=====	=====	=====	=====
UPPER LIMIT						
=====	=====	=====	=====	=====	=====	=====
LOWER LIMIT						
=====	=====	=====	=====	=====	=====	=====
EPA SAMPLE NO.						
=====	=====	=====	=====	=====	=====	=====
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (BCM) = Bromochloromethane
 IS2 (DFB) = 1,4-Difluorobenzene
 IS3 (CBZ) = Chlorobenzene-d5
 UPPER LIMIT = + 100% of internal standard area.
 LOWER LIMIT = - 50% of internal standard area.

Column used to flag internal standard area values with an asterisk

page ___ of ___

8B
SEMIVOLATILE INTERNAL STANDARD AREA SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Lab File ID (Standard): _____ Date Analyzed: _____
 Instrument ID: _____ Time Analyzed: _____

	IS1 (DCB) AREA #	RT	IS2 (NPT) AREA #	RT	IS3 (ANT) AREA #	RT
=====	=====	=====	=====	=====	=====	=====
12 HOUR STD						
=====	=====	=====	=====	=====	=====	=====
UPPER LIMIT						
=====	=====	=====	=====	=====	=====	=====
LOWER LIMIT						
=====	=====	=====	=====	=====	=====	=====
EPA SAMPLE NO.						
=====	=====	=====	=====	=====	=====	=====
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						

IS1 (DCB) = 1,4-Dichlorobenzene-d4
 IS2 (NPT) = Naphthalene-d8
 IS3 (ANT) = Acenaphthene-d10

UPPER LIMIT = + 100%
 of internal standard area.
 LOWER LIMIT = - 50%
 of internal standard area.

Column used to flag internal standard area values with an asterisk

8D
PESTICIDE EVALUATION STANDARDS SUMMARY

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Instrument ID: _____ GC Column ID: _____
 Dates of Analyses: _____ to _____

Evaluation Check for Linearity

PESTICIDE	CALIBRATION FACTOR EVAL MIX A	CALIBRATION FACTOR EVAL MIX B	CALIBRATION FACTOR EVAL MIX C	%RSD (\leq 10.0%)
Aldrin				
Endrin				
4,4'-DDT				
DBC				

(1)

(1) If > 10.0% RSD, plot a standard curve and determine the ng for each sample in that set from the curve.

Evaluation Check for 4,4'-DDT/Endrin Breakdown
(percent breakdown expressed as total degradation)

	DATE ANALYZED	TIME ANALYZED	ENDRIN	4,4'-DDT	COMBINED (2)
INITIAL					
01 EVAL MIX B					
02 EVAL MIX B					
03 EVAL MIX B					
04 EVAL MIX B					
05 EVAL MIX B					
06 EVAL MIX B					
07 EVAL MIX B					
08 EVAL MIX B					
09 EVAL MIX B					
10 EVAL MIX B					
11 EVAL MIX B					
12 EVAL MIX B					
13 EVAL MIX B					
14 EVAL MIX B					

(2) See Form instructions.

8E
 PESTICIDE EVALUATION STANDARDS SUMMARY
 Evaluation of Retention Time Shift for Dibutylchloroendate

Lab Name: _____ Contract: _____
 Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____
 Instrument ID: _____ GC Column ID: _____
 Dates of Analyses: _____ to _____

	EPA SAMPLE NO.	LAB SAMPLE ID	DATE ANALYZED	TIME ANALYZED	% D	*
01						
02						
03						
04						
05						
06						
07						
08						
09						
10						
11						
12						
13						
14						
15						
16						
17						
18						
19						
20						
21						
22						
23						
24						
25						
26						
27						
28						
29						
30						
31						
32						
33						
34						
35						
36						
37						
38						

* Values outside of QC limits (2.0% for packed columns,
 0.3% for capillary columns)

9
PESTICIDE/PCB STANDARDS SUMMARY

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

Instrument ID: _____ GC Column ID: _____

DATE(S) OF ANALYSIS	DATE OF ANALYSIS
FROM: _____	_____
TO: _____	_____
TIME(S) OF ANALYSIS	TIME OF ANALYSIS
FROM: _____	_____
TO: _____	_____
	EPA SAMPLE NO. _____
	(STANDARD) _____

COMPOUND	RT	RT WINDOW		CALIBRATION FACTOR	RT	CALIBRATION FACTOR	QNT Y/N	%D
		FROM	TO					
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Hept. epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endo. sulfate								
4,4'-DDT								
Methoxychlor								
Endrin ketone								
a. Chlordane								
g. Chlordane								
Toxaphene								
Aroclor-1016								
Aroclor-1221								
Aroclor-1232								
Aroclor-1242								
Aroclor-1248								
Aroclor-1254								
Aroclor-1260								

Under QNT Y/N: enter Y if quantitation was performed, N if not performed.
%D must be less than or equal to 15.0% for quantitation, and less than or equal to 20.0% for confirmation.

Note: Determining that no compounds were found above the CRQL is a form of quantitation, and therefore at least one column must meet the 15.0% criteria.

For multicomponent analytes, the single largest peak that is characteristic of the component should be used to establish retention time and %D. Identification of such analytes is based primarily on pattern recognition.

10
PESTICIDE/PCB IDENTIFICATION

EPA SAMPLE NO.

Lab Name: _____ Contract: _____

Lab Code: _____ Case No.: _____ SAS No.: _____ SDG No.: _____

GC Column ID (1): _____ GC Column ID (2): _____

Instrument ID (1): _____ Instrument ID (2): _____

Lab Sample ID: _____

Lab File ID: _____ (only if confirmed by GC/MS)

PESTICIDE/PCB	RETENTION TIME	RT WINDOW OF STANDARD		QUANT? (Y/N)	GC/MS? (Y/N)
		From	TO		
01 _____	Column 1 _____	_____	_____	-	-
02 _____	Column 2 _____	_____	_____	-	-
03 _____	Column 1 _____	_____	_____	-	-
04 _____	Column 2 _____	_____	_____	-	-
05 _____	Column 1 _____	_____	_____	-	-
06 _____	Column 2 _____	_____	_____	-	-
07 _____	Column 1 _____	_____	_____	-	-
08 _____	Column 2 _____	_____	_____	-	-
09 _____	Column 1 _____	_____	_____	-	-
10 _____	Column 2 _____	_____	_____	-	-
11 _____	Column 1 _____	_____	_____	-	-
12 _____	Column 2 _____	_____	_____	-	-

Comments: _____

CHAPTER TWO

CHOOSING THE CORRECT PROCEDURE

2.1 PURPOSE

This chapter aids the analyst in choosing the appropriate methods for samples, based upon sample matrix and the analytes to be determined.

2.1.1 Trace Analysis vs. Macroanalysis

The methods presented in SW-846 were designed through sample sizing and concentration procedures to address the problem of "trace" analyses (<1000 ppm), and have been developed for an optimized working range. These methods are also applicable to "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses, as well as to "trace" analyses, through use of appropriate sample preparation techniques that result in analyte concentration within that optimized range. Such sample preparation techniques include:

- 1) adjustment of size of sample prepared for analysis,
- 2) adjustment of injection volumes,
- 3) dilution or concentration of sample,
- 4) elimination of concentration steps prescribed for "trace" analyses,
- 5) direct injection (of samples to be analyzed for volatile constituents).

The performance data presented in each of these methods were generated from "trace" analyses, and may not be applicable to "minor" and "major" analyses. Generally, extraction efficiency improves as concentration increases.

CAUTION: Care should be taken when analyzing samples for trace analyses subsequent to analysis of concentrated samples due to the possibility of contamination.

2.1.2 Choice of Apparatus and Preparation of Reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, those specified in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

2.2 REQUIRED INFORMATION

In order to choose the correct combination of methods to form the appropriate analytical procedure, some basic information is required.

2.2.1 Physical State(s) of Sample

The phase characteristics of the sample must be known. There are several general categories of phases in which the sample may be categorized:

Aqueous
Sludges
Multiphase Samples
Ground Water

Oil and Organic Liquid
Solids
EP and TCLP Extracts

2.2.2 Analytes

Analytes are divided into classes based on the determinative methods which are used to identify and quantify them. Table 2-1 lists the organic analytes of SW-846 methods, Table 2-2 lists the analytes that may be prepared using Method 3650, and Table 2-3 lists the analytes that are collected from stack gas effluents using VOST methodology. Tables 2-4 through 2-31 list the target analytes of each organic determinative method. Some of the analytes appear on more than one table, as they may be determined using any of several methods. Table 2-32 indicates which methods are applicable to inorganic target analytes.

2.2.3 Detection Limits Required

Regulations may require a specific sensitivity or detection limit for an analysis, as in the determination of analytes for the Toxicity Characteristic (TC) or for delisting petitions. Drinking water detection limits, for those specific organic and metallic analytes covered by the National Interim Primary Drinking Water Standards, are desired in the analysis of ground water.

2.2.4 Analytical Objective

Knowledge of the analytical objective will be useful in the choice of aliquoting procedures and in the selection of a determinative method. This is especially true when the sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be transmitted to the analytical laboratory management to ensure that the correct techniques are being applied to the analytical effort.

2.2.5 Detection and Monitoring

The strategy for detection of compounds in environmental or process samples may be contrasted with the strategy for monitoring samples. Detection samples define initial conditions. When there is little information available about the composition of the sample source, e.g., a well or process stream, mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of detection for organic analytes, given the analytical requirements, is mass spectral identification. The choice of technique for metals is governed by the detection limit requirements and potential interferences.

Monitoring samples, on the other hand, are analyzed to confirm existing and on-going conditions, tracking the presence or absence of constituents in an environmental or process matrix. A less compound(s)-specific detection mode may be used because the matrix and the analytical conditions are well defined and stable.

2.2.6 Sample Containers, Preservations, and Holding Times

Appropriate sample containers, sample preservation techniques, and sample holding times for aqueous matrices are listed in Table 2-32, near the end of this chapter. Similar information may be found in Table 3-1 of Chapter Three (inorganic analytes) and Table 4-1 of Chapter Four (organic analytes). Samples must be extracted/analyzed within the specified holding times for the results to be considered reflective of total concentrations. Analytical data generated outside of the specified holding times must be considered to be minimum values only. Such data may be used to demonstrate that a waste is hazardous where it shows the concentration of a constituent to be above the regulatory threshold but cannot be used to demonstrate that a waste is not hazardous.

2.3 IMPLEMENTING THE GUIDANCE

The choice of the appropriate sequence of methods depends on the information required and on the experience of the analyst. Figure 2-1 summarizes the organic analysis options available. Appropriate selection is confirmed by the quality control results. The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

2.3.1 Extraction and Sample Preparation Procedures

Methods for preparing organic analytes are shown in Table 2-34. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

2.3.1.1 Aqueous Samples

The choice of a preparative method depends on the sample. Methods 3510 and 3520 may be used for extraction of the semivolatile organic compounds. Method 3510, a separatory funnel extraction, is appropriate for samples which will not form a persistent emulsion interphase between the sample and the extraction solvent. The formation of an emulsion that cannot be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a liquid-liquid continuous extraction, may be used for any aqueous sample; this method will minimize emulsion formation.

2.3.1.1.1 Basic or Neutral Extraction of Semivolatiles

The solvent extract obtained by performing either Method 3510 or 3520 at a neutral or basic pH will contain the compounds of interest. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the pH requirements for extraction prior to analysis.

2.3.1.1.2 Acidic Extraction of Phenols and Acids

The extract obtained by performing either Method 3510 or 3520 at a pH less than or equal to 2 will contain the phenols and acid extractables.

2.3.1.2 Solid Samples

Soxhlet (Method 3540) and ultrasonic (Method 3550) extractions are used with solid samples. Consolidated samples should be ground finely enough to pass through a 1 mm sieve. In limited applications, waste dilution (Method 3580) may be used if the entire sample is soluble in the specified solvent.

Method 3540 and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent detection of the analytes of interest. This separation will be most important if a GC method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

2.3.1.3 Oils and Organic Liquids

Method 3580, waste dilution, may be used and the resultant sample analyzed directly by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Method 3580 gives guidance on performing waste dilutions.

To remove interferences, Method 3611 may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

2.3.1.4 Sludge Samples

There is no set ratio of liquid to solid which enables the analyst to determine which of the three extraction methods cited is the most appropriate. If the sludge is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definition of sludges with

respect to the relative percent of liquid and solid components. They may be classified into three categories but with appreciable overlap.

2.3.1.4.1 Liquids

Use of Method 3510 or Method 3520 may be applicable to sludges that behave like and have the consistency of aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet (Method 3540) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.1.4.2 Solids

Soxhlet (Method 3540) and ultrasonic extraction (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.1.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions.

1. Freezing/thawing: Certain emulsions will separate if exposed to temperatures below 0°C.
2. Salting out: Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.
3. Centrifugation: Centrifugal force may separate emulsion components by density.
4. Addition of water or ethanol: Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.1.5 Multiphase Samples

Choice of the procedure for aliquoting multiphase samples is very dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared with Figure 2-1 and Tables 2-34 through 2-36 for further guidance.

2.3.2 Cleanup Procedures

Each category in Table 2-35, Cleanup of Organic Analyte Extracts, corresponds to one of the possible determinative methods available in the manual. Cleanups employed are determined by the analytes of interest within the extract. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst's discretion must determine the necessity for cleanup procedures, as there are no clear cut criteria for indicating their use. Method 3600 and associated methods should be consulted for further details on extract cleanup.

2.3.3 Determinative Procedures

The determinative methods for organic analytes have been divided into three categories, shown in Table 2-36: gas chromatography/mass spectrometry (GC/MS); specific detection methods, i.e., gas chromatography (GC); and high performance liquid chromatography (HPLC). This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers have been indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific detection method.

Method 8000 gives a general description of the technique of gas chromatography. This method should be consulted prior to application of any of the gas chromatographic methods.

Method 8080, for organochlorine pesticides and polychlorinated biphenyls, Method 8140 and 8141, for organophosphorus pesticides, and Methods 8150 and 8151, for chlorinated herbicides, are preferred over GC/MS because of the combination

of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

Methods 8240 and 8260 are both GC/MS methods for volatile analytes. Method 8240 uses a packed column whereas Method 8260 employs a capillary column. Better chromatographic separation of the volatile compounds may be obtained by using Method 8260 rather than 8240. Performance criteria will be based on Method 8260. Method 5030 has been combined with both Method 8240 and 8260, with which it was used exclusively. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, described in Section 2.2.5.

Methods 8250 and 8270 are both GC/MS methods for semivolatile analytes. Method 8250 uses a packed column whereas Method 8270 employs a capillary column. Better chromatographic separation of the semivolatile compounds may be obtained by using Method 8270 rather than 8250. Performance criteria will be based on Method 8270.

2.4 CHARACTERISTICS

Figure 2-2 outlines a sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

2.4.1 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-3A) or the TCLP (Figure 2-3B) is an aqueous sample, and therefore, requires further solvent extraction prior to the analysis of semivolatile compounds.

The TCLP leachate is solvent extracted with methylene chloride at a pH > 11 by either Method 3510 or 3520. Method 3510 should be used unless the formation of emulsions between the sample and the solvent prevent proper extraction. If this problem is encountered, Method 3520 should be employed.

The solvent extract obtained by performing either Method 3510 or 3520 at a basic or neutral pH will contain the base/neutral compounds of interest. Refer to the specific determinative method for guidance on the pH requirements for extraction prior to analysis.

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap be used to introduce the volatile sample into the gas chromatograph.

2.5 GROUND WATER

Appropriate analysis schemes for the determination of analytes in ground water are presented in Figures 2-4A, 2-4B, and 2-4C. Quantitation limits for the metallic analytes should correspond to the drinking water limits which are available.

2.5.1 Special Techniques for Metal Analytes

All atomic absorption analyses should employ appropriate background correction systems whenever spectral interferences could be present. Several background correction techniques are employed in modern atomic absorption spectrometers. Matrix modification can complement background correction in some cases. Since no approach to interference correction is completely effective in all cases, the analyst should attempt to verify the adequacy of correction. If the interferant is known (e.g. high concentrations of iron in the determination of selenium), accurate analyses of synthetic solutions of the interferant (with and without analyte) could establish the efficacy of the background correction. If the nature of the interferant is not established, good agreement of analytical results using two substantially different wavelengths could substantiate the adequacy of the background correction.

To reduce matrix interferences, all graphite furnace atomic absorption (GFAA) analyses should be performed using techniques which maximize an isothermal environment within the furnace cell. Data indicate that two such techniques, L'vov platform and the Delayed Atomization Cuvette (DAC), are equivalent in this respect, and produce high quality results.

Cadmium and antimony should be determined by GFAA. These two elements are analyzed by GFAA to achieve lower detection limits. Typical GFAA detection limits for antimony and cadmium are 3 $\mu\text{g/L}$ and 0.1 $\mu\text{g/L}$, compared to 60 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$ by ICP.

All furnace atomic absorption analysis should be carried out using the exact matrix modifiers listed below. (See also the appropriate methods.)

<u>Element(s)</u>	<u>Modifier</u>
As and Se	Nickel Nitrate
Pb	Phosphoric Acid
Cd	Ammonium Phosphate
Sb	Ammonium Nitrate
Tl	Platinum/Palladium

The ICP calibration standards must match the acid composition and strength of the acids contained in the samples. Acid strengths in the ICP calibration standards should be stated in the raw data.

2.5.2 Special Techniques for Indicated Analytes and Anions

If an Auto-Analyzer is used to read the cyanide distillates, the spectrophotometer must be used with a 50 mm path length cell. If a sample is found to contain cyanide, the sample must be redistilled a second time and analyzed to confirm the presence of the cyanide. The second distillation must fall within the 14 day holding time.

2.6 REFERENCES

1. Barcelona, M.J. "TOC Determinations in Ground Water"; Ground Water 1984, 22(1), 18-24.
2. Riggan, R.; et al. Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-008.
3. McKee, G.; et al. Determination of Inorganic Anions in Water by Ion Chromatography; (Technical addition to Methods for Chemical Analysis of Water and Wastewater, EPA 600/4-79-020), U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1984; EPA-600/4-84-017.

TABLE 2-1
DETERMINATIVE ANALYTICAL METHODS FOR ORGANIC COMPOUNDS

Compound	Applicable Method(s)
Acenaphthene	8100, 8250/8270, 8310, 8410
Acenaphthylene	8100, 8250/8270, 8310, 8410
Acetaldehyde	8315
Acetone	8240/8260, 8315
Acetonitrile	8240/8260
Acetophenone	8250/8270
2-Acetylaminofluorene	8270
1-Acetyl-2-thiourea	8270
Acifluorfen	8151
Acrolein (Propenal)	8030, 8240/8260, 8315, 8316
Acrylamide	8032, 8316
Acrylonitrile	8030, 8031, 8240/8260, 8316
Alachlor	8081
Aldicarb (Temik)	8318
Aldicarb Sulfone	8318
Aldrin	8080/8081, 8250/8270, 8275
Allyl alcohol	8240/8260
Allyl chloride	8010, 8240/8260
2-Aminoanthraquinone	8270
Aminoazobenzene	8270
4-Aminobiphenyl	8250/8270
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	8330
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	8330
3-Amino-9-ethylcarbazole	8270
Anilazine	8270
Aniline	8250/8270
o-Anisidine	8270
Anthracene	8100, 8250/8270, 8310, 8410
Aramite	8270
Aroclor-1016 (PCB-1016)	8080/8081, 8250/8270
Aroclor-1221 (PCB-1221)	8080/8081, 8250/8270
Aroclor-1232 (PCB-1232)	8080/8081, 8250/8270
Aroclor-1242 (PCB-1242)	8080/8081, 8250/8270
Aroclor-1248 (PCB-1248)	8080/8081, 8250/8270
Aroclor-1254 (PCB-1254)	8080/8081, 8250/8270
Aroclor-1260 (PCB-1260)	8080/8081, 8250/8270
Aspona	8141
Asulam	8321
Atrazine	8141
Azinphos-ethyl	8141
Azinphos-methyl	8140/8141, 8270
Barban	8270
Bentazon	8151
Benzal chloride	8121

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Benzaldehyde	8315
Benz(a)anthracene	8100, 8250/8270, 8310, 8410
Benzene	8020, 8021, 8240/8260
Benzidine	8250/8270
Benzoic acid	8250/8270, 8410
Benzo(b)fluoranthene	8100, 8250/8270, 8310
Benzo(j)fluoranthene	8100
Benzo(k)fluoranthene	8100, 8250/8270, 8275, 8310
Benzo(g,h,i)perylene	8100, 8250/8270, 8310
Benzo(a)pyrene	8100, 8250/8270, 8275, 8310, 8410
p-Benzoquinone	8270
Benzotrichloride	8121
Benzyl alcohol	8250/8270
Benzyl benzoate	8061
Benzyl chloride	8010, 8121, 8240/8260
BHC (Hexachlorocyclohexane)	8120
γ-BHC (alpha-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
β-BHC (beta-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
γ-BHC (Lindane, gamma-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
δ-BHC (delta-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
Bolstar (Sulprofos)	8140/8141
Bromoacetone	8010, 8240/8260
Bromobenzene	8010, 8021, 8260
Bromochloromethane	8021, 8240/8260
Bromodichloromethane	8010, 8021, 8240/8260
4-Bromofluorobenzene	8240/8260
Bromoform	8010, 8021, 8240/8260
Bromomethane	8010, 8021, 8240/8260
4-Bromophenyl phenyl ether	8110, 8250/8270, 8410
Bromoxynil	8270
Butanal	8315
n-Butanol	8260
2-Butanone (Methyl ethyl ketone, MEK)	8015, 8240/8260
n-Butylbenzene	8021, 8260
sec-Butylbenzene	8021, 8260
tert-Butylbenzene	8021, 8260
Butyl benzyl phthalate	8060/8061, 8250/8270, 8410
2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	8040, 8150/8151, 8270, 8321
Captafol	8081, 8270
Captan	8081, 8270
Carbaryl (Sevin)	8270, 8318
Carbazole	8275
Carbofuran (Furaden)	8270, 8318

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Carbon disulfide	8240/8260
Carbon tetrachloride	8010, 8021, 8240/8260
Carbophenothion (Carbofenthion)	8141, 8270
Chloral hydrate	8240/8260
Chloramben	8151
Chlordane	8080, 8250/8270
α -Chlordane	8081
γ -Chlordane	8081
Chlorfenvinphos	8141, 8270
Chloroacetaldehyde	8010
Chloroacetonitrile	8260
4-Chloroaniline	8250/8270, 8410
Chlorobenzene	8010, 8020, 8021, 8240/8260
Chlorobenzilate	8081, 8270
2-Chloro-1,3-butadiene	8260
1-Chlorobutane	8260
Chlorodibromomethane (Dibromochloromethane)	8010, 8021, 8240/8260
Chloroethane	8010, 8021, 8240/8260
2-Chloroethanol	8010, 8240/8260
bis(2-Chloroethoxy)methane	8010, 8110, 8250/8270, 8410
bis(2-Chloroethyl)ether	8110, 8250/8270, 8410
bis(2-Chloroethyl)sulfide	8240/8260
2-Chloroethyl vinyl ether	8010, 8240/8260
Chloroform	8010, 8021, 8240/8260
1-Chlorohexane	8010, 8260
bis(2-Chloroisopropyl) ether	8010, 8110, 8250/8270, 8410
Chloromethane	8010, 8021, 8240/8260
5-Chloro-2-methylaniline	8270
Chloromethyl methyl ether	8010
4-Chloro-3-methylphenol	8040, 8250/8270, 8275, 8410
Chloroneb	8081
3-(Chloromethyl)pyridine hydrochloride	8270
1-Chloronaphthalene	8250/8270, 8275
2-Chloronaphthalene	8120/8121, 8250/8270, 8410
2-Chlorophenol	8040, 8250/8270, 8275, 8410
4-Chlorophenol	8410
4-Chloro-1,2-phenylenediamine	8270
4-Chloro-1,3-phenylenediamine	8270
4-Chlorophenyl phenyl ether	8110, 8250/8270, 8410
Chloroprene	8010, 8240/8260
3-Chloropropene	8260
3-Chloropropionitrile	8240/8260
Chloropropylate	8081
Chlorothalonil	8081

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
1-Chlorotoluene	8021, 8260
2-Chlorotoluene	8010, 8021, 8260
Chlorpyrifos	8140/8141
Chlorpyrifos methyl	8141
Chrysene	8100, 8250/8270, 8310, 8410
Coumaphos	8140/8141, 8270
Coumarin Dyes	8321
o-Cresidine	8270
o-Cresol (2-Methylphenol)	8250/8270, 8410
m-Cresol (3-Methylphenol)	8270
p-Cresol (4-Methylphenol)	8250/8270, 8275, 8410
Cresols (Methylphenols, Cresylic acids)	8040
Crotonaldehyde	8260, 8315
Crotoxyphos	8141, 8270
Cyclohexanone	8315
1-Cyclohexyl-4,6-dinitrophenol	8040, 8270
1,4-D	8150/8151, 8321
Dalapon	8150/8151, 8321
1,4-DB	8150/8151, 8321
DACP	8081
2,4-D, butoxyethanol ester	8321
DCPA	8081
DCPA diacid	8151
2,4'-DDD	8080/8081, 8250/8270
2,4'-DDE	8080/8081, 8270
2,4'-DDT	8080/8081, 8250/8270
Decanal	8315
Demeton-O, and -S	8140/8141, 8270
2,4-D,ethylhexyl ester	8321
Diallate	8081, 8270
2,4-Diaminotoluene	8270
Diazinon	8140/8141
Dibenz(a,h)acridine	8100
Dibenz(a,h)anthracene	8100, 8250/8270, 8310
Dibenz(a,j)acridine	8100, 8250/8270
7H-Dibenzo(c,g)carbazole	8100
Dibenzofuran	8250/8270, 8410
Dibenzo(a,e)pyrene	8100, 8270
Dibenzo(a,h)pyrene	8100
Dibenzo(a,i)pyrene	8100
Dibenzothiophene	8275
Dibromochloromethane (Chlorodibromomethane)	8010, 8021, 8240/8260
1,2-Dibromo-3-chloropropane	8010, 8011, 8240/8260, 8270
1,2-Dibromoethane (Ethylene dibromide)	8010, 8011, 8021, 8240/8260

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Dibromofluoromethane	8260
Dibromomethane	8010, 8021, 8240/8260
tris(2,3-Dibromopropyl) phosphate (Tris-BP)	8270, 8321
Di-n-butyl phthalate	8060/8061, 8250/8270, 8410
Dicamba	8150/8151, 8321
Dichlone	8081, 8270
1,2-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
1,3-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
1,4-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
3,3'-Dichlorobenzidine	8250/8270
3,5-Dichlorobenzoic acid	8151
1,4-Dichloro-2-butene	8010, 8240
cis-1,4-Dichloro-2-butene	8260
trans-1,4-Dichloro-2-butene	8260
Dichlorodifluoromethane	8010, 8021, 8240/8260
1,1-Dichloroethane	8010, 8021, 8240/8260
1,2-Dichloroethane	8010, 8021, 8240/8260
1,1-Dichloroethene (Vinylidene chloride)	8010, 8021, 8240/8260
cis-1,2-Dichloroethene	8021, 8260
trans-1,2-Dichloroethene	8010, 8021, 8240/8260
Dichlorofenthion	8141
Dichloromethane (Methylene chloride)	8010, 8021, 8240/8260
2,4-Dichlorophenol	8040, 8250/8270, 8275, 8410
2,6-Dichlorophenol	8040, 8250/8270
Dichlorprop	8150/8151, 8321
1,2-Dichloropropane	8010, 8021, 8240/8260
1,3-Dichloropropane	8021, 8260
2,2-Dichloropropane	8021, 8260
1,3-Dichloro-2-propanol	8010, 8240/8260
1,1-Dichloropropene	8021, 8260
cis-1,3-Dichloropropene	8010, 8021, 8240/8260
trans-1,3-Dichloropropene	8010, 8021, 8240/8260
Dichlorvos (Dichlorovos)	8140/8141, 8270, 8321
Dichrotophos	8141, 8270
Dicofol	8081
Dieldrin	8080/8081, 8250/8270
1,2,3,4-Diepoxybutane	8240/8260
Diethyl ether	8015, 8260
Diethyl phthalate	8060/8061, 8250/8270, 8410
Diethylstilbestrol	8270
Diethyl sulfate	8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
1,4-Difluorobenzene	8240/8260
Dihydrosaffrole	8270
Dimethoate	8141, 8270, 8321
3,3'-Dimethoxybenzidine	8270
Dimethylaminoazobenzene	8250/8270
2,5-Dimethylbenzaldehyde	8315
7,12-Dimethylbenz(a)anthracene	8250/8270
3,3'-Dimethylbenzidine	8270
γ , α -Dimethylphenethylamine	8250/8270
2,4-Dimethylphenol	8040, 8250/8270
Dimethyl phthalate	8060/8061, 8250/8270, 8410
Dinitrobenzene	8090
1,2-Dinitrobenzene	8270
1,3-Dinitrobenzene (1,3-DNB)	8270, 8330
1,4-Dinitrobenzene	8270
1,6-Dinitro-2-methylphenol	8250/8270, 8410
2,4-Dinitrophenol	8040, 8250/8270, 8410
2,4-Dinitrotoluene (2,4-DNT)	8090, 8250/8270, 8275, 8330, 8410
2,6-Dinitrotoluene (2,6-DNT)	8090, 8250/8270, 8330, 8410
Di-n-cap	8270
Di-noseb (2-sec-Butyl-4,6-dinitrophenol, DNBP)	8040, 8150/8151, 8270, 8321
Di-n-octyl phthalate	8060/8061, 8250/8270, 8410
Di-n-propyl phthalate	8410
Dioxacarb	8318
1,4-Dioxane	8240/8260
Dioxathion	8141, 8270
Diphenylamine	8250/8270, 8275
5,5-Diphenylhydantoin	8270
1,2-Diphenylhydrazine	8250/8270
Disperse Blue 3	8321
Disperse Blue 14	8321
Disperse Brown 1	8321
Disperse Orange 3	8321
Disperse Orange 30	8321
Disperse Red 1	8321
Disperse Red 5	8321
Disperse Red 13	8321
Disperse Red 60	8321
Disperse Yellow 5	8321
Disulfoton	8140/8141, 8270, 8321
Endosulfan I	8080/8081, 8250/8270
Endosulfan II	8080/8081, 8250/8270
Endosulfan sulfate	8080/8081, 8250/8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Endrin	8080/8081, 8250/8270
Endrin aldehyde	8080/8081, 8250/8270
Endrin ketone	8081, 8250/8270
Epichlorohydrin	8010, 8240/8260
EPN	8141, 8270
Ethion	8141, 8270
Ethoprop	8140/8141
Ethyl acetate	8260
Ethylbenzene	8020, 8021, 8240/8260
Ethyl carbamate	8270
Ethylene dibromide	8010, 8011, 8021, 8240/8260
Ethylene oxide	8240/8260
bis(2-Ethylhexyl) phthalate	8060/8061, 8250/8270, 8410
Ethyl methacrylate	8240/8260
Ethyl methanesulfonate	8250/8270
Ethyl parathion	8270
Etridiazole	8081
Famphur	8141, 8270, 8321
Fenithrothion	8141
Fensulfothion	8140/8141, 8270, 8321
Fenthion	8140/8141, 8270
Fluchloralin	8270
Fluoranthene	8100, 8250/8270, 8310, 8410
Fluorene	8100, 8250/8270, 8275, 8310, 8410
Fluorescent Brightener 61	8321
Fluorescent Brightener 236	8321
Fluorobenzene	8260
2-Fluorobiphenyl	8250/8270
2-Fluorophenol	8250/8270
Fonophos	8141
Formaldehyde	8315
Halowax-1000	8081
Halowax-1001	8081
Halowax-1013	8081
Halowax-1014	8081
Halowax-1051	8081
Halowax-1099	8081
Heptachlor	8080/8081, 8250/8270
Heptachlor epoxide	8080/8081, 8250/8270
Heptanal	8315
Hexachlorobenzene	8081, 8120/8121, 8250/8270, 8275, 8410

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Hexachlorobutadiene (1,3-Hexachlorobutadiene)	8021, 8120/8121, 8250/8270, 8260, 8410
Hexachlorocyclohexane	8120
Hexachlorocyclopentadiene	8081, 8120/8121, 8250/8270, 8410
Hexachloroethane	8120/8121, 8250/8270, 8260, 8410
Hexachlorophene	8270
Hexachloropropene	8270
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8330
Hexamethylphosphoramide (HMPA)	8141, 8270
Hexanal	8315
2-Hexanone	8240/8260
HMX	8330
1,2,3,4,6,7,8-HpCDD	8280/8290
1,2,3,4,6,7,8-HpCDF	8280/8290
1,2,3,4,7,8,9-HpCDF	8280/8290
1,2,3,4,7,8-HxCDD	8280/8290
1,2,3,6,7,8-HxCDD	8280/8290
1,2,3,7,8,9-HxCDD	8280/8290
1,2,3,4,7,8-HxCDF	8280/8290
1,2,3,6,7,8-HxCDF	8280/8290
1,2,3,7,8,9-HxCDF	8280/8290
2,3,4,6,7,8-HxCDF	8280/8290
Hydroquinone	8270
3-Hydroxycarbofuran	8318
5-Hydroxydicamba	8151
2-Hydroxypropionitrile	8240/8260
Indeno(1,2,3-cd)pyrene	8100, 8250/8270, 8310
Iodomethane	8240/8260
Isobutyl alcohol (2-Methyl-1-propanol)	8240/8260
Isodrin	8081, 8270
Isophorone	8090, 8250/8270, 8410
Isopropylbenzene	8021, 8260
p-Isopropyltoluene	8021, 8260
Isosafrole	8270
Isovaleraldehyde	8315
Kepone	8081, 8270
Leptophos	8141, 8270
Malathion	8141, 8270
Maleic anhydride	8270
Malononitrile	8240/8260
MCPA	8150/8151, 8321
MCPP	8150/8151, 8321

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Merphos	8140/8141, 8321
Mestranol	8270
Methacrylonitrile	8240/8260
Methanol	8260
Methapyrilene	8270
Methiocarb (Mesurol)	8318
Methomyl (Lannate)	8318, 8321
Methoxychlor (4,4'-Methoxychlor)	8080/8081, 8250/8270
Methyl acrylate	8260
Methyl-t-butyl ether	8260
3-Methylcholanthrene	8100, 8250/8270
2-Methyl-4,6-dinitrophenol	8040
4,4'-Methylenebis(2-chloroaniline)	8270
4,4'-Methylenebis(N,N-dimethylaniline)	8270
Methyl ethyl ketone (MEK, 2-Butanone)	8015, 8240/8260
Methylene chloride (Dichloromethane)	8010, 8021, 8240/8260
Methyl iodide	8010, 8240/8260
Methyl isobutyl ketone (4-Methyl-2-pentanone)	8015, 8240/8260
Methyl methacrylate	8240/8260
Methyl methanesulfonate	8250/8270
2-Methylnaphthalene	8250/8270, 8410
2-Methyl-5-nitroaniline	8270
Methyl parathion	8270, 8321
4-Methyl-2-pentanone (Methyl isobutyl ketone)	8015, 8240/8260
2-Methylphenol (o-Cresol)	8250/8270, 8410
3-Methylphenol (m-Cresol)	8270
4-Methylphenol (p-Cresol)	8250/8270, 8275, 8410
2-Methylpyridine	8270
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	8330
Mevinphos	8140/8141, 8270
Mexacarbate	8270
Mirex	8081, 8270
Monochrotophos	8141, 8270, 8321
Naled	8140/8141, 8270, 8321
Naphthalene	8021, 8100, 8250/8270, 8260, 8275, 8310, 8410
Naphthoquinone	8090
1,4-Naphthoquinone	8270
1-Naphthylamine	8250/8270
2-Naphthylamine	8250/8270
Nicotine	8270
5-Nitroacenaphthene	8270
2-Nitroaniline	8250/8270, 8410
3-Nitroaniline	8250/8270, 8410

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
4-Nitroaniline	8250/8270, 8410
5-Nitro-o-anisidine	8270
Nitrobenzene (NB)	8090, 8250/8270, 8260, 8330, 8410
4-Nitrobiphenyl	8270
Nitrofen	8081, 8270
2-Nitrophenol	8040, 8250/8270, 8410
4-Nitrophenol	8040, 8151, 8250/8270, 8410
2-Nitropropane	8260
Nitroquinoline-1-oxide	8270
N-Nitrosodibutylamine	8250/8270
N-Nitrosodiethylamine	8270
N-Nitrosodimethylamine	8070, 8250/8270, 8410
N-Nitrosodiphenylamine	8070, 8250/8270, 8410
N-Nitrosodi-n-propylamine	8070, 8250/8270, 8410
N-Nitrosomethylethylamine	8270
N-Nitrosomorpholine	8270
N-Nitrosopiperidine	8250/8270
N-Nitrosopyrrolidine	8270
o-Nitrotoluene (2-NT)	8330
m-Nitrotoluene (3-NT)	8330
p-Nitrotoluene (4-NT)	8330
5-Nitro-o-toluidine	8270
trans-Nonachlor	8081
Nonanal	8315
OCDD	8280
OCDF	8280
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8330
Octamethyl pyrophosphoramidate	8270
Octanal	8315
4,4'-Oxydianiline	8270
Parathion	8270
Parathion, ethyl	8141
Parathion, methyl	8140/8141
PCB-1016 (Aroclor-1016)	8080/8081, 8250/8270
PCB-1221 (Aroclor-1221)	8080/8081, 8250/8270
PCB-1232 (Aroclor-1232)	8080/8081, 8250/8270
PCB-1242 (Aroclor-1242)	8080/8081, 8250/8270
PCB-1248 (Aroclor-1248)	8080/8081, 8250/8270
PCB-1254 (Aroclor-1254)	8080/8081, 8250/8270
PCB-1260 (Aroclor-1260)	8080/8081, 8250/8270
PCNB	8081
1,2,3,4,7-PeCDD	8280

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
1,2,3,7,8-PeCDD	8280/8290
1,2,3,7,8-PeCDF	8280/8290
2,3,4,7,8-PeCDF	8280/8290
Pentachlorobenzene	8121, 8250/8270
Pentachloroethane	8240/8260
Pentachlorohexane	8120
Pentachloronitrobenzene	8250/8270
Pentachlorophenol	8040, 8151, 8250/8270, 8410
Pentafluorobenzene	8260
Pentanal	8315
trans-Permethrin	8081
Perthane	8081
Phenacetin	8250/8270
Phenanthrene	8100, 8250/8270, 8275, 8310, 8410
Phenobarbital	8270
Phenol	8040, 8250/8270, 8410
1,4-Phenylenediamine	8270
Phorate	8140/8141, 8270, 8321
Phosalone	8270
Phosmet	8141, 8270
Phosphamidion	8141, 8270
Phthalic anhydride	8270
Picloram	8151
2-Picoline	8240/8260, 8250/8270
Piperonyl sulfoxide	8270
Promecarb	8318
Pronamide	8250/8270
Propachlor	8081
Propanal	8315
Propargyl alcohol	8240/8260
β-Propiolactone	8240/8260
Propionitrile	8240/8260
Propoxur (Baygon)	8318
n-Propylamine	8240/8260
n-Propylbenzene	8021, 8260
Propylthiouracil	8270
Pyrene	8100, 8250/8270, 8275, 8310, 8410
Pyridine	8240/8260, 8270
RDX	8330
Resorcinol	8270
Ronnel	8140/8141
Safrole	8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Simazine	8141
Solvent Red 3	8321
Solvent Red 23	8321
Stirophos (Tetrachlorvinphos)	8140/8141, 8270
Strobane	8081
Strychnine	8270, 8321
Styrene	8021, 8240/8260
Sulfallate	8270
Sulfotep	8141
2,4,5-T	8150/8151, 8321
2,4,5-T, butoxyethanol ester	8321
2,4,5-T, butyl ester	8321
1,2,3,4-TCDD	8280
1,2,7,8-TCDD	8280
1,2,8,9-TCDD	8280
1,3,6,8-TCDD	8280
1,3,7,8-TCDD	8280
1,3,7,9-TCDD	8280
2,3,7,8-TCDD	8280/8290
1,2,7,8-TCDF	8280
2,3,7,8-TCDF	8280/8290
TEPP	8141
Terbufos (Terbufos)	8141, 8270
1,2,3,4-Tetrachlorobenzene	8121
1,2,3,5-Tetrachlorobenzene	8121
1,2,4,5-Tetrachlorobenzene	8121, 8250/8270
Tetrachlorobenzenes	8120
1,1,1,2-Tetrachloroethane	8010, 8021, 8240/8260
1,1,2,2-Tetrachloroethane	8010, 8021, 8240/8260
Tetrachloroethene	8010, 8021, 8240/8260
2,3,4,6-Tetrachlorophenol	8250/8270
Tetrachlorophenols	8040
Tetrachlorvinphos (Stirophos)	8140/8141, 8270
Tetraethyl dithiopyrophosphate	8270
Tetraethyl pyrophosphate	8270
Tetrazene	8331
Thiofanox	8321
Thionazine	8141, 8270
Thiophenol (Benzenethiol)	8270
TOCP (Tri-o-cresylphosphate)	8141
Tokuthion (Prothiofos)	8140/8141
m-Tolualdehyde	8315
o-Tolualdehyde	8315
p-Tolualdehyde	8315

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Toluene	8020, 8021, 8240/8260
Toluene diisocyanate	8270
o-Toluidine	8270
Toxaphene	8080/8081, 8250/8270
2,4,5-TP (Silvex)	8150/8151, 8321
2,4,6-Tribromophenol	8250/8270
1,2,3-Trichlorobenzene	8021, 8121, 8260
1,2,4-Trichlorobenzene	8021, 8120/8121, 8250/8270, 8260, 8410
1,3,5-Trichlorobenzene	8121
1,1,1-Trichloroethane	8010, 8021, 8240/8260
1,1,2-Trichloroethane	8010, 8021, 8240/8260
Trichloroethene	8010, 8021, 8240/8260
Trichlorofluoromethane	8010, 8021, 8240/8260
Trichlorfon	8141, 8321
Trichloronate	8140/8141
2,4,5-Trichlorophenol	8250/8270, 8410
2,4,6-Trichlorophenol	8040, 8250/8270, 8410
Trichlorophenols	8040
1,2,3-Trichloropropane	8010, 8021, 8240/8260
0,0,0-Triethyl phosphorothioate	8270
Trifluralin	8081, 8270
2,4,5-Trimethylaniline	8270
1,2,4-Trimethylbenzene	8021, 8260
1,3,5-Trimethylbenzene	8021, 8260
Trimethyl phosphate	8270
1,3,5-Trinitrobenzene (1,3,5-TNB)	8270, 8330
2,4,6-Trinitrotoluene (2,4,6-TNT)	8330
Tri-o-cresyl phosphate (TOCP)	8141
Tri-p-tolyl phosphate	8270
Vinyl acetate	8240/8260
Vinyl chloride	8010, 8021, 8240/8260
o-Xylene	8021, 8260
m-Xylene	8021, 8260
p-Xylene	8021, 8260
Xylene (Total)	8020, 8240

TABLE 2-2A.
METHOD 3650 - BASE/NEUTRAL FRACTION

Benz(a)anthracene	Hexachlorobenzene
Benzo(a)pyrene	Hexachlorobutadiene
Benzo(b)fluoranthene	Hexachloroethane
Chlordane	Hexachlorocyclopentadiene
Chlorinated dibenzodioxins	Naphthalene
Chrysene	Nitrobenzene
Creosote	Phorate
Dichlorobenzene(s)	2-Picoline
Dinitrobenzene	Pyridine
2,4-Dinitrotoluene	Tetrachlorobenzene(s)
Heptachlor	Toxaphene

TABLE 2-2B.
METHOD 3650 - ACID FRACTION

2-Chlorophenol	4-Nitrophenol
Cresol(s)	Pentachlorophenol
Creosote	Phenol
Dichlorophenoxyacetic acid	Tetrachlorophenol(s)
2,4-Dimethylphenol	Trichlorophenol(s)
4,6-Dinitro-o-cresol	2,4,5-TP (Silvex)

TABLE 2-3.
METHOD 5041 - SORBENT CARTRIDGES FROM
VOLATILE ORGANIC SAMPLING TRAIN (VOST)

Acetone	1,2-Dichloropropane
Acrylonitrile	cis-1,3-Dichloropropene
Benzene	trans-1,3-Dichloropropene
Bromodichloromethane	Ethylbenzene ^a
Bromoform ^a	Iodomethane
Bromomethane ^b	Methylene chloride
Carbon disulfide	Styrene ^a
Carbon tetrachloride	1,1,2,2-Tetrachloroethane ^a
Chlorobenzene	Tetrachloroethene
Chlorodibromomethane	Toluene
Chloroethane ^b	1,1,1-Trichloroethane
Chloroform	1,1,2-Trichloroethane
Chloromethane ^b	Trichloroethene
Dibromomethane	Trichlorofluoromethane
1,1-Dichloroethane	1,2,3-Trichloropropane ^a
1,2-Dichloroethane	Vinyl chloride ^b
1,1-Dichloroethene	Xylenes ^a
trans-1,2-Dichloroethene	

^a Boiling point of this compound is above 132°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

^b Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Section 1.3 of Method 5041 for discussion.

TABLE 2-4.
METHOD 8010 - HALOGENATED VOLATILES

Allyl chloride	1,3-Dichlorobenzene
Benzyl chloride	1,4-Dichlorobenzene
Bromoacetone	1,4-Dichloro-2-butene
Bromobenzene	Dichlorodifluoromethane
Bromodichloromethane	1,1-Dichloroethane
Bromoform	1,2-Dichloroethane
Bromomethane	1,1-Dichloroethene (Vinylidene chloride)
Carbon tetrachloride	trans-1,2-Dichloroethene
Chloroacetaldehyde	Dichloromethane (Methylene Chloride)
Chlorobenzene	1,2-Dichloropropane
Chloroethane	1,3-Dichloro-2-propanol
bis(2-Chloroethoxy)methane	cis-1,3-Dichloropropene
2-Chloroethanol	trans-1,3-Dichloropropene
2-Chloroethyl vinyl ether	Epichlorhydrin
Chloroform	Ethylene dibromide
1-Chlorohexane	Methyl iodide
bis(2-Chloroisopropyl) ether	1,1,2,2-Tetrachloroethane
Chloromethane	1,1,1,2-Tetrachloroethane
Chloromethyl methyl ether	Tetrachloroethene
Chloroprene	1,1,1-Trichloroethane
4-Chlorotoluene	1,1,2-Trichloroethane
Dibromochloromethane	Trichloroethene
1,2-Dibromo-3-chloropropane	Trichlorofluoromethane
Dibromomethane	1,2,3-Trichloropropane
1,2-Dichlorobenzene	Vinyl chloride

TABLE 2-5.
METHOD 8015 - NONHALOGENATED VOLATILES

Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)

TABLE 2-6.
METHOD 8020 - AROMATIC VOLATILES

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethylbenzene
Toluene
Xylenes

TABLE 2-7.
METHOD 8021 (METHOD 8011*) - HALOGENATED AND AROMATIC VOLATILES

Benzene	1,3-Dichloropropane
Bromobenzene	2,2-Dichloropropane
Bromochloromethane	1,1-Dichloropropene
Bromodichloromethane	cis-1,3-Dichloropropene
Bromoform	trans-1,3-Dichloropropene
Bromomethane	Ethylbenzene
n-Butylbenzene	Hexachlorobutadiene
sec-Butylbenzene	Isopropylbenzene
tert-Butylbenzene	p-Isopropyltoluene
Carbon tetrachloride	Methylene chloride
Chlorobenzene	Naphthalene
Chlorodibromomethane	n-Propylbenzene
Chloroethane	Styrene
Chloroform	1,1,1,2-Tetrachloroethane
Chloromethane	1,1,2,2-Tetrachloroethane
2-Chlorotoluene	Tetrachloroethene
4-Chlorotoluene	Toluene
1,2-Dibromo-3-chloropropane*	1,2,3-Trichlorobenzene
1,2-Dibromoethane*	1,2,4-Trichlorobenzene
Dibromomethane	1,1,1-Trichloroethane
1,2-Dichlorobenzene	1,1,2-Trichloroethane
1,3-Dichlorobenzene	Trichloroethene
1,4-Dichlorobenzene	Trichlorofluoromethane
Dichlorodifluoromethane	1,2,3-Trichloropropane
1,1-Dichloroethane	1,2,4-Trimethylbenzene
1,2-Dichloroethane	1,3,5-Trimethylbenzene
1,1-Dichloroethene	Vinyl chloride
cis-1,2-Dichloroethene	o-Xylene
trans-1,2-Dichloroethene	m-Xylene
1,2-Dichloropropane	p-Xylene

* Indicates the only two target analytes of Method 8011. These constituents are also target analytes of Method 8021.

Table 2-8.
METHODS 8030/8031 -
ACROLEIN, ACRYLONITRILE

Acrolein (Propenal)*
Acrylonitrile

* Target analyte of Method 8030 only.

TABLE 2-9
METHOD 8032 -
ACRYLAMIDE

Acrylamide

TABLE 2-10.
METHOD 8040 - PHENOLS

2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	2-Methyl-4,6-dinitrophenol
4-Chloro-3-methylphenol	2-Nitrophenol
2-Chlorophenol	4-Nitrophenol
Cresols (Methylphenols)	Pentachlorophenol
2-Cyclohexyl-4,6-dinitrophenol	Phenol
2,4-Dichlorophenol	Tetrachlorophenols
2,6-Dichlorophenol	2,4,6-Trichlorophenol
2,4-Dimethylphenol	Trichlorophenols
2,4-Dinitrophenol	

TABLE 2-11.
METHODS 8060/8061 - PHTHALATE ESTERS

BenzyI benzoate*
Butyl benzyI phthalate
Bis(2-ethylhexyl) phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

* Target analyte of Method 8061 only.

TABLE 2-12.
METHOD 8070 - NITROSAMINES

N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine

TABLE 2-13.
METHODS 8080/8081 - ORGANOCHLORINE PESTICIDES AND PCBs

Aroclor-1016 (PCB-1016)	Chloropropylate*	Halowax-1014*
Aroclor-1221 (PCB-1221)	Chlorothalonil*	Halowax-1051*
Aroclor-1232 (PCB-1232)	DCBP*	Halowax-1099*
Aroclor-1242 (PCB-1242)	DCPA*	Heptachlor
Aroclor-1248 (PCB-1248)	Diallate*	Heptachlor epoxide
Aroclor-1254 (PCB-1254)	Dichlone*	Hexachlorobenzene*
Aroclor-1260 (PCB-1260)	Dicofol*	Hexachlorocyclo-
Alachlor*	4,4'-DDD	pentadiene*
Aldrin	4,4'-DDE	Isodrin*
α -BHC	4,4'-DDT	Kepone*
β -BHC	Dieldrin	4,4'-Methoxychlor
δ -BHC	Endosulfan I	Mirex*
γ -BHC (Lindane)	Endosulfan II	Nitrofen*
Captafol*	Endosulfan sulfate	PCNB*
Captan*	Endrin	Perthane*
Chlorobenzilate*	Endrin aldehyde	Propachlor*
Chlordane**	Endrin ketone*	Strobane*
α -Chlorodane*	Etridiazole*	Toxaphene
γ -Chlorodane*	Halowax-1000*	trans-Nonachlor*
Chloroneb*	Halowax-1001*	trans-Permethrin*
	Halowax-1013*	Trifluralin*

* Target analyte of Method 8081 only.

** Target analyte of Method 8080 only.

TABLE 2-14.
METHOD 8090 - NITROAROMATICS AND
CYCLIC KETONES

Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Naphthoquinone
Nitrobenzene

TABLE 2-15.
METHODS 8100 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	7H-Dibenzo(c,g)carbazole
Acenaphthylene	Dibenzo(a,e)pyrene
Anthracene	Dibenzo(a,h)pyrene
Benzo(a)anthracene	Dibenzo(a,i)pyrene
Benzo(a)pyrene	Fluoranthene
Benzo(b)fluoranthene	Fluorene
Benzo(j)fluoranthene	Indeno(1,2,3-cd)pyrene
Benzo(k)fluoranthene	3-Methylcholanthrene
Benzo(g,h,i)perylene	Naphthalene
Chrysene	Phenanthrene
Dibenz(a,h)acridine	Pyrene
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	

TABLE 2-16
METHOD 8110 - HALOETHERS

bis(2-Chloroethyl) ether	4-Bromophenyl phenyl ether
bis(2-Chloroethoxy)methane	4-Chlorophenyl phenyl ether
bis(2-Chloroisopropyl) ether	

TABLE 2-17.
METHODS 8120/8121 - CHLORINATED HYDROCARBONS

Benzal chloride*	gamma-Hexachlorocyclohexane (gamma-BHC)*
Benzotrichloride*	delta-Hexachlorocyclohexane (delta-BHC)*
Benzyl chloride*	Hexachlorocyclopentadiene
2-Chloronaphthalene	Hexachloroethane
1,2-Dichlorobenzene	Pentachlorobenzene*
1,3-Dichlorobenzene	Pentachlorohexane**
1,4-Dichlorobenzene	Tetrachlorobenzenes**
Hexachlorobenzene	1,2,3,4-Tetrachlorobenzene*
Hexachlorobutadiene	1,2,3,5-Tetrachlorobenzene*
Hexachlorocyclohexane**	1,2,4,5-Tetrachlorobenzene*
alpha-Hexachlorocyclohexane (alpha-BHC)*	1,2,3-Trichlorobenzene*
beta-Hexachlorocyclohexane (beta-BHC)*	1,2,4-Trichlorobenzene
	1,3,5-Trichlorobenzene*

* Target analyte of Method 8121 only.

** Target analyte of Method 8120 only.

TABLE 2-18.
METHODS 8140/8141 - ORGANOPHOSPHORUS COMPOUNDS
(PACKED AND CAPILLARY COLUMNS)

Aspon*	Fenthion
Atrazine*	Fonophos*
Azinphos ethyl*	Hexamethylphosphoramide*
Azinphos methyl	(HMPA)
Bolstar (Sulprofos)	Leptophos*
Carbophenothion*	Malathion*
Chlorofenvinphos*	Merphos
Chlorpyrifos	Mevinphos
Chlorpyrifos methyl*	Monochrotophos*
Coumaphos	Naled
Crotoxypos*	Parathion, ethyl*
Demeton-O, and -S	Parathion, methyl
Diazinon	Phorate
Dichlorofenthion*	Phosmet*
Dichlorvos (DDVP)	Phosphamidon*
Dichrotophos*	Ronnel
Dimethoate*	Simazine*
Dioxathion*	Stirophos (Tetrachlorvinphos)
Disulfoton	Sulfotepp*
EPN*	TEPP*
Ethion*	Terbufos*
Ethoprop	Thionazin*
Famphur*	Tri-o-cresylphosphate (TOCP)*
Fenithrothion*	Tokuthion (Prothiofos)
Fensulfothion	Trichlorfon*
	Trichloronate

* Target analyte of Method 8141 only.

TABLE 2-19.
METHODS 8150/8151 - CHLORINATED HERBICIDES

Acifluorfen*	Dicamba	MCPA
Bentazon*	3,5-Dichlorobenzoic acid*	MCPP
Chloramben*	Dichlorprop	4-Nitrophenol*
2,4-D	Dinoseb	Pentachlorophenol*
Dalapon	5-Hydroxydicamba*	Picloram*
2,4-DB		2,4,5-TP (Silvex)
DCPA diacid*		2,4,5-T

* Target analyte of Method 8151 only.

TABLE 2-20.
METHODS 8240/8260 - VOLATILES

Acetone	1,2-Dibromo-3-chloropropane	Isopropylbenzene*
Acetonitrile	1,2-Dibromoethane	p-Isopropyltoluene*
Acrolein (Propenal)	Dibromomethane	Malononitrile
Acrylonitrile	Dibromofluoromethane*	Methacrylonitrile
Allyl alcohol	1,2-Dichlorobenzene*	Methanol*
Allyl chloride	1,3-Dichlorobenzene*	Methyl acrylate*
Benzene	1,4-Dichlorobenzene*	Methyl-t-butyl ether*
Benzyl chloride	1,4-Dichloro-2-butene	Methylene chloride
Bromoacetone	cis-1,4-Dichloro-2-butene*	Methyl iodide
Bromobenzene*	trans-1,4-Dichloro-2-butene*	Methyl methacrylate
Bromochloromethane	1,4-Dichloro-2-butene**	4-Methyl-2-pentanone (MIBK)
Bromodichloromethane	Dichlorodifluoromethane	Naphthalene*
4-Bromofluorobenzene	1,1-Dichloroethane	Nitrobenzene*
Bromoform	1,2-Dichloroethane	2-Nitropropane*
Bromomethane	1,1-Dichloroethene	Pentachloroethane
n-Butanol*	cis-1,2-Dichloroethene*	Pentafluorobenzene*
2-Butanone (Methyl ethyl ketone)	trans-1,2-Dichloroethene	2-Picoline
n-Butylbenzene*	1,2-Dichloropropane	Propargyl alcohol
sec-Butylbenzene*	1,3-Dichloropropane*	β-Propiolactone
tert-Butylbenzene*	2,2-Dichloropropane*	Propionitrile
Carbon disulfide	1,3-Dichloro-2-propanol	n-Propylamine
Carbon tetrachloride	1,1-Dichloropropene*	n-Propylbenzene*
Chloral hydrate	cis-1,3-Dichloropropene	Pyridine
Chloroacetonitrile*	trans-1,3-Dichloropropene	Styrene
Chlorobenzene	1,2,3,4-Diepoxybutane	1,1,1,2-Tetrachloroethane
2-Chloro-1,3-butadiene*	Diethyl ether*	1,1,2,2-Tetrachloroethane
1-Chlorobutane*	1,4-Difluorobenzene	Tetrachloroethene
Chlorodibromomethane	1,4-Dioxane	Toluene
Chloroethane	Epichlorohydrin	1,2,3-Trichlorobenzene*
2-Chloroethanol	Ethanol	1,2,4-Trichlorobenzene*
bis(2-Chloroethyl) sulfide	Ethyl acetate*	1,1,1-Trichloroethane
2-Chloroethyl vinyl ether	Ethylbenzene	1,1,2-Trichloroethane
Chloroform	Ethylene oxide	Trichloroethene
1-Chlorohexane*	Ethyl methacrylate	Trichlorofluoromethane
Chloromethane	Fluorobenzene*	1,2,3-Trichloropropane
Chloroprene	Hexachlorobutadiene*	1,2,4-Trimethylbenzene*
3-Chloropropene*	Hexachloroethane*	1,3,5-Trimethylbenzene*
3-Chloropropionitrile	2-Hexanone	Vinyl acetate
2-Chlorotoluene*	2-Hydroxypropionitrile	Vinyl chloride
4-Chlorotoluene*	Iodomethane	Xylene (Total)**
Crotonaldehyde*	Isobutyl alcohol	o-Xylene*
		m-Xylene*
		p-Xylene*

* Target analyte of Method 8260 only.

** Target analyte of Method 8240 only.

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES

Acenaphthene	Carbophenothion*
Acenaphthylene	Chlordane
Acetophenone	Chlorfenvinphos*
2-Acetylaminofluorene*	4-Chloroaniline
1-Acetyl-2-thiourea*	Chlorobenzilate*
Aldrin	5-Chloro-2-methylaniline*
2-Aminoanthraquinone*	4-Chloro-3-methylphenol
Aminoazobenzene*	3-(Chloromethyl)pyridine hydrochloride*
4-Aminobiphenyl	1-Chloronaphthalene
3-Amino-9-ethylcarbazole*	2-Chloronaphthalene
Anilazine*	2-Chlorophenol
Aniline	4-Chloro-1,2-phenylenediamine*
o-Anisidine*	4-Chloro-1,3-phenylenediamine*
Anthracene	4-Chlorophenyl phenyl ether
Aramite*	Chrysene
Aroclor-1016	Coumaphos*
Aroclor-1221	p-Cresidine*
Aroclor-1232	Crotoxyphos*
Aroclor-1242	2-Cyclohexyl-4,6-dinitrophenol*
Aroclor-1248	4,4'-DDD
Aroclor-1254	4,4'-DDE*
Aroclor-1260	4,4'-DDT
Azinphos-methyl*	Demeton-O*
Barban*	Demeton-S*
Benz(a)anthracene	Diallate (cis or trans)*
Benzidine	2,4-Diaminotoluene*
Benzo(b)fluoranthene	Dibenz(a,j)acridine
Benzo(k)fluoranthene	Dibenz(a,h)anthracene
Benzoic acid	Dibenzofuran
Benzo(g,h,i)perylene	Dibenzo(a,e)pyrene*
Benzo(a)pyrene	1,2-Dibromo-3-chloropropane*
p-Benzoquinone*	Di-n-butyl phthalate
Benzyl alcohol	Dichlone*
α-BHC	1,2-Dichlorobenzene
β-BHC	1,3-Dichlorobenzene
δ-BHC	1,4-Dichlorobenzene
γ-BHC (Lindane)	3,3'-Dichlorobenzidine
Bis(2-chloroethoxy)methane	2,4-Dichlorophenol
Bis(2-chloroethyl) ether	2,6-Dichlorophenol
Bis(2-chloroisopropyl) ether	Dichlorovos*
Bis(2-ethylhexyl) phthalate	Dicrotophos*
4-Bromophenyl phenyl ether	Dieldrin
Bromoxynil*	Diethyl phthalate
Butyl benzyl phthalate	Diethylstilbestrol*
2-sec-Butyl-4,6-dinitrophenol (Dinoseb)*	Diethyl sulfate*
Captafol*	Dihydrosaffrole*
Captan*	Dimethoate*
Carbaryl*	3,3'-Dimethoxybenzidine*
Carbofuran*	Dimethylaminoazobenzene

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

7,12-Dimethylbenz(a)anthracene	Indeno(1,2,3-cd)pyrene
3,3'-Dimethylbenzidine*	Isodrin*
α,α -Dimethylphenethylamine	Isophorone
2,4-Dimethylphenol	Isosafrole*
Dimethyl phthalate	Kepone*
1,2-Dinitrobenzene*	Leptophos*
1,3-Dinitrobenzene*	Malathion*
1,4-Dinitrobenzene*	Maleic Anhydride*
4,6-Dinitro-2-methylphenol	Mestranol*
2,4-Dinitrophenol	Methapyrilene*
2,4-Dinitrotoluene	Methoxychlor
2,6-Dinitrotoluene	3-Methylcholanthrene
Dinocap*	4,4'-Methylenebis(2-chloroaniline)*
Dioxathion*	4,4'-Methylenebis(N,N-dimethylaniline)*
Diphenylamine	Methyl methanesulfonate
5,5-Diphenylhydantoin*	2-Methylnaphthalene
1,2-Diphenylhydrazine	2-Methyl-5-nitroaniline*
Di-n-octyl phthalate	Methyl parathion*
Disulfoton*	2-Methylphenol (o-Cresol)
Endosulfan I	3-Methylphenol (m-Cresol)*
Endosulfan II	4-Methylphenol (p-Cresol)
Endosulfan sulfate	2-Methylpyridine*
Endrin	Mevinphos*
Endrin aldehyde	Mexacarbate*
Endrin ketone	Mirex*
EPN*	Monocrotophos*
Ethion*	Naled*
Ethyl carbamate*	Naphthalene
Ethyl methanesulfonate	1,4-Naphthoquinone*
Ethyl parathion*	1-Naphthylamine
Famphur*	2-Naphthylamine
Fensulfothion*	Nicotine*
Fenthion*	5-Nitroacenaphthene*
Fluchloralin*	2-Nitroaniline
Fluoranthene	3-Nitroaniline
Fluorene	4-Nitroaniline
2-Fluorobiphenyl	5-Nitro-o-anisidine*
2-Fluorophenol	Nitrobenzene
Heptachlor	4-Nitrobiphenyl*
Heptachlor epoxide	Nitrofen*
Hexachlorobenzene	2-Nitrophenol
Hexachlorobutadiene	4-Nitrophenol
Hexachlorocyclopentadiene	Nitroquinoline-1-oxide*
Hexachloroethane	N-Nitrosodibutylamine
Hexachlorophene*	N-Nitrosodiethylamine*
Hexachloropropene*	N-Nitrosodimethylamine
Hexamethylphosphoramide*	N-Nitrosodiphenylamine
Hydroquinone*	N-Nitrosodi-n-propylamine

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

N-Nitrosomethylethylamine*	Terbuphos*
N-Nitrosomorpholine*	1,2,4,5-Tetrachlorobenzene
N-Nitrosopiperidine	2,3,4,6-Tetrachlorophenol
N-Nitrosopyrrolidine*	Tetrachlorvinphos (Stirophos)*
5-Nitro-o-toluidine*	Tetraethyl dithiopyrophosphate*
Octamethyl pyrophosphoramidate*	Tetraethyl pyrophosphate*
4,4'-Oxydianiline*	Thionazine*
Parathion*	Thiophenol (Benzenethiol)*
Pentachlorobenzene	Toluene diisocyanate*
Pentachloronitrobenzene	o-Toluidine*
Pentachlorophenol	Toxaphene
Phenacetin	2,4,6-Tribromophenol
Phenanthrene	1,2,4-Trichlorobenzene
Phenobarbital*	2,4,5-Trichlorophenol
Phenol	2,4,6-Trichlorophenol
1,4-Phenylenediamine*	Trifluralin*
Phorate*	2,4,5-Trimethylaniline*
Phosalone*	Trimethyl phosphate*
Phosmet*	1,3,5-Trinitrobenzene*
Phosphamidion*	Tris(2,3-dibromopropyl) phosphate*
Phthalic anhydride*	Tri-p-tolyl phosphate*
2-Picoline	0,0,0-Triethyl phosphorothioate*
Piperonyl sulfoxide*	
Pronamide	
Propylthiouracil*	
Pyrene	
Pyridine*	
Resorcinol*	
Safrole*	
Strychnine*	
Sulfallate*	

* Target analyte of Method 8270 only.

TABLE 2-22.
METHOD 8275 - SEMIVOLATILES (SCREENING)

2-Chlorophenol	2,4-Dinitrotoluene	Carbazole
4-Methylphenol	Fluorene	Aldrin
2,4-Dichlorophenol	Diphenylamine	Pyrene
Naphthalene	Hexachlorobenzene	Benzo(k)fluoranthene
4-Chloro-3-methylphenol	Dibenzothiophene	Benzo(a)pyrene
1-Chloronaphthalene	Phenanthrene	

TABLE 2-23.
METHODS 8280/8290 - DIOXINS AND DIBENZOFURANS

2,3,7,8-TCDD	1,2,3,4,7-PeCDD*	1,2,7,8-TCDF*
1,2,3,4-TCDD*	1,2,3,7,8-PeCDD	2,3,7,8-TCDF
1,3,6,8-TCDD*	1,2,3,4,7,8-HxCDD	1,2,3,7,8-PeCDF
1,3,7,9-TCDD*	1,2,3,6,7,8-HxCDD	2,3,4,7,8-PeCDF
1,3,7,8-TCDD*	1,2,3,7,8,9-HxCDD	1,2,3,4,7,8-HxCDF
1,2,7,8-TCDD*	1,2,3,4,6,7,8-HpCDD	1,2,3,6,7,8-HxCDF
1,2,8,9-TCDD*	OCDD*	1,2,3,7,8,9-HxCDF
		2,3,4,6,7,8-HxCDF
		1,2,3,4,6,7,8-HpCDF
		1,2,3,4,7,8,9-HpCDF
		OCDF*

* Target analyte of 8280 only

TABLE 2-24.
METHOD 8310 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

TABLE 2-25.
METHOD 8315 - CARBONYL COMPOUNDS

Acetaldehyde	Heptanal
Acetone	Hexanal (Hexaldehyde)
Acrolein	Isovaleraldehyde
Benzaldehyde	Nonanal
Butanal (Butyraldehyde)	Octanal
Crotonaldehyde	Pentanal (Valeraldehyde)
Cyclohexanone	Propanal (Propionaldehyde)
Decanal	m-Tolualdehyde
2,5-Dimethylbenzaldehyde	o-Tolualdehyde
Formaldehyde	p-Tolualdehyde

TABLE 2-26.
METHOD 8316 - ACRYLAMIDE,
ACRYLONITRILE AND ACROLEIN

Acrylamide
Acrylonitrile
Acrolein

TABLE 2-27.
METHOD 8318 - N-METHYLCARBAMATES

Aldicarb (Temik)
Aldicarb Sulfone
Carbaryl (Sevin)
Carbofuran (Furadan)
Dioxacarb
3-Hydroxycarbofuran
Methiocarb (MesuroI)
Methomyl (Lannate)
Promecarb
Propoxur (Baygon)

TABLE 2-28.
METHOD 8321 - NONVOLATILES

Azo Dyes
Disperse Red 1
Disperse Red 5
Disperse Red 13
Disperse Yellow 5
Disperse Orange 3
Disperse Orange 30
Disperse Brown 1
Solvent Red 3
Solvent Red 23

Anthraquinone Dyes
Disperse Blue 3
Disperse Blue 14
Disperse Red 60
Coumarin Dyes

(Fluorescent Brighteners)
Fluorescent Brightener 61
Fluorescent Brightener 236

Chlorinated Phenoxyacid Compounds

Dalapon
Dicamba
2,4-D
MCPA
MCP
Dichlorprop
2,4,5-T
Silvex (2,4,5-TP)
Dinoseb
2,4-DB
2,4-D, butoxyethanol ester
2,4-D, ethylhexyl ester
2,4,5-T, butyl ester
2,4,5-T, butoxyethanol ester

Alkaloids
Caffeine
Strychnine

Organophosphorus Compounds

Methomyl
Thiofanox
Famphur
Asulam
Dichlorvos
Dimethoate
Disulfoton
Fensulfotion
Merphos
Methyl parathion
Monocrotophos
Naled
Phorate
Trichlorfon
tris-(2,3-Dibromopropyl) phosphate,
(Tris-BP)

TABLE 2-29.
METHOD 8330 - NITROAROMATICS AND NITRAMINES

Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
1,3,5-Trinitrobenzene (1,3,5-TNB)
1,3-Dinitrobenzene (1,3-DNB)
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)
Nitrobenzene (NB)
2,4,6-Trinitrotoluene (2,4,6-TNT)
4-Amino-2,6-dinitrotoluene (4-Am-DNT)
2-Amino-4,6-dinitrotoluene (2-Am-DNT)
2,4-Dinitrotoluene (2,4-DNT)
2,6-Dinitrotoluene (2,6-DNT)
2-Nitrotoluene (2-NT)
3-Nitrotoluene (3-NT)
4-Nitrotoluene (4-NT)

TABLE 2-30.
METHOD 8331 - TETRAZENE

Tetrazene

TABLE 2-31
METHOD 8410 - SEMIVOLATILES

Acenaphthene	2,4-Dinitrotoluene
Acenaphthylene	2,6-Dinitrotoluene
Anthracene	Di-n-octyl phthalate
Benzo(a)anthracene	Fluoranthene
Benzo(b)pyrene	Fluorene
Benzoic acid	Hexachlorobenzene
Bis(2-chloroethoxy)methane	1,3-Hexachlorobutadiene
Bis(2-chloroethyl)ether	Hexachlorocyclopentadiene
Bis(2-chloroisopropyl)ether	Hexachloroethane
Bis(2-ethylhexyl)phthalate	Isophorone
4-Bromophenyl phenyl ether	2-Methylnaphthalene
Butyl benzyl phthalate	2-Methylphenol
4-Chloroaniline	4-Methylphenol
4-Chloro-3-methylphenol	Naphthalene
2-Chloronaphthalene	2-Nitroaniline
2-Chlorophenol	3-Nitroaniline
4-Chlorophenol	4-Nitroaniline
4-Chlorophenyl phenyl ether	Nitrobenzene
Chrysene	2-Nitrophenol
Dibenzofuran	4-Nitrophenol
1,2-Dichlorobenzene	N-Nitrosodimethylamine
1,3-Dichlorobenzene	N-Nitrosodiphenylamine
1,4-Dichlorobenzene	N-Nitroso-di-n-propylamine
2,4-Dichlorophenol	Pentachlorophenol
Diethyl phthalate	Phenanthrene
Dimethyl phthalate	Phenol
Di-n-butyl phthalate	Pyrene
Di-n-propyl phthalate	1,2,4-Trichlorobenzene
4,6-Dinitro-2-methylphenol	2,4,5-Trichlorophenol
2,4-Dinitrophenol	2,4,6-Trichlorophenol

TABLE 2-32.
ANALYSIS METHODS FOR INORGANIC COMPOUNDS

Compound	Applicable Method(s)
Aluminum	6010, 6020, 7020
Antimony	6010, 6020, 7040, 7041, 7062
Arsenic	6010, 6020, 7060, 7061, 7062
Barium	6010, 6020, 7080, 7081
Beryllium	6010, 6020, 7090, 7091
Bromide	9056
Cadmium	6010, 6020, 7130, 7131
Calcium	6010, 7140
Chloride	9056, 9250, 9251, 9252, 9253
Chromium	6010, 6020, 7190, 7191
Chromium, hexavalent	7195, 7196, 7197, 7198
Cobalt	6010, 6020, 7200, 7201
Copper	6010, 6020, 7210, 7211
Cyanide	9010, 9012, 9013
Fluoride	9056
Iron	6010, 7380, 7381
Lead	6010, 6020, 7420, 7421
Lithium	6010, 7430
Magnesium	6010, 7450
Manganese	6010, 6020, 7460, 7461
Mercury	7470, 7471
Molybdenum	6010, 7480, 7481
Nickel	6010, 6020, 7520
Nitrate	9056, 9200
Nitrite	9056
Osmium	7550
Phosphate	9056
Phosphorus	6010
Potassium	6010, 7610
Selenium	6010, 7740, 7741, 7742
Silver	6010, 6020, 7760, 7761
Sodium	6010, 7770
Strontium	6010, 7780
Sulfate	9035, 9036, 9038, 9056
Sulfide	9030, 9031
Thallium	6010, 6020, 7840, 7841
Tin	7870
Vanadium	6010, 7910, 7911
Zinc	6010, 6020, 7950, 7951

TABLE 2-33.
CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES^A

Name	Container ¹	Preservation	Maximum holding time
Bacterial Tests:			
Coliform, total	P, G	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃	6 hours
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool, 4°C; if oxidizing agents present add 5 mL 0.1N NaAsO ₂ per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH. See Method 9010 for other interferences.	14 days
Hydrogen ion (pH)	P, G	None required	24 hours
Nitrate	P, G	Cool, 4°C	48 hours
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C, add zinc acetate	7 days
Metals:			
Chromium VI	P, G	Cool, 4°C	24 hours
Mercury	P, G	HNO ₃ to pH<2	28 days
Metals, except chromium VI and mercury	P, G	HNO ₃ to pH<2	6 months
Organic Tests:			
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³ , Adjust pH to 4-5	14 days
Benzidines	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³ , Adjust pH to 6-9, store in dark	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³	7 days until extraction, 40 days after extraction
Dioxins and Furans	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³ , store in dark	7 days until extraction, 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³ , store in dark	7 days until extraction, 40 days after extraction
Oil and grease	G	Cool, 4°C ²	28 days
Organic carbon, total (TOC)	P, G	Cool, 4°C ²	28 days
PCBs	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Pesticides	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Phenols	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³	7 days until extraction, 40 days after extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³ , store in dark	7 days until extraction, 40 days after extraction
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ^{2,3}	14 days
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% Na ₂ S ₂ O ₃ ³	14 days
Total organic halides (TOX)	G, Teflon-lined cap	Cool, 4°C ²	28 days
Radiological Tests:			
Alpha, beta and radium	P, G	HNO ₃ to pH<2	6 months

^A Table excerpted, in part, from Table II, 49 FR 209, October 26, 1984, p 28.

¹ Polyethylene (P) or Glass (G)

² Adjust to pH<2 with H₂SO₄, HCl or solid NaHSO₄.

³ Free chlorine must be removed prior to addition of HCl by the appropriate addition of Na₂S₂O₃.

Table 2-34.
PREPARATION METHODS FOR ORGANIC ANALYTES

	Aqueous (pH) ³	Solids	Sludges Emulsions ¹ (pH) ³	Oils
Acids	3510 3520 (<2)	3540 3550 3580 ²	3520 (<2)	3650 3580 ²
Acrolein Acrylonitrile Acetonitrile	5030	5030	5030	5030
Aromatic Volatiles	5030	5030	5030	5030
Base/Neutral	3510 3520 (>11)	3540 3550 3580 ²	3520 (>11)	3650 3580 ²
Chlorinated Herbicides	8150 (<2)	8150 3580 ²	8150 (<2)	3580 ²
Chlorinated Hydrocarbons	3510 3520 (Neutral)	3540 3550 3580 ²	3520 (Neutral)	3580 ²
Halogenated Volatiles	5030	5030	5030	5030
Nitroaromatic and Cyclic Ketones	3510 3520 (5-9)	3540 3550 3580 ²	3520 (5-9)	3580 ²
Non-halogenated Volatiles	5030	5030	5030	5030
Organochlorine Pesticides and PCBs	3510 3520 3665 (5-9)	3540 3550 3580 ² 3665 3541*	3520 (5-9)	3580 ²
Organophosphorus Pesticides	3510 3520 (6-8)	3540 3550 3580 ²	3520 (6-8)	3580 ²
Phenols	3510 3520 (<2)	3540 3550 3580 ²	3520 (<2)	3650 3580 ²
Phthalate Esters	3510 3520 (Neutral)	3540 3550 3580 ²	3520 (Neutral)	3580 ²
Polynuclear Aromatic Hydrocarbons	3510 3520 (Neutral)	3540 3550 3580 ²	3520 (Neutral)	3560 3580 ²
Volatile Organics	5030	5030	5030	5030

¹ If attempts to break up emulsions are unsuccessful, these methods may be used.

² Waste dilution, Method 3580, is only appropriate if the sample is soluble in the specified solvent.

³ pH at which extraction should be performed.

*Method 3541 is appropriate if the sample is to be analyzed for PCBs only.

TABLE 2-35.
CLEANUP OF ORGANIC ANALYTE EXTRACTS

Analyte Type	Method(s)
Acids	3650
Base/Neutral	3650
Chlorinated Herbicides	8150
Chlorinated Hydrocarbons	3620 3640
Nitroaromatics & Cyclic Ketones	3620 3640
Organophosphorus Pesticides	3620
Organochlorine Pesticides & PCBs	3620 3640 3660 3665
Phenols	3630 3640 3650
Phthalate Esters	3610 3620 3640
Polynuclear Aromatic Hydrocarbons	3611 3630 3640

**TABLE 2-36.
DETERMINATION OF ORGANIC ANALYTES**

	GC/MS Determination Methods	Specific GC Detection Methods	HPLC
SEMIVOLATILES			
Acids	8270 8250		
Base/Neutral	8270 8250		
Carbamates			8318
Chlorinated Herbicides	8270*	8150 8151	
Chlorinated Hydrocarbons	8270 8250	8120 8121	
Dyes			8321
Explosives			8330 8331
Haloethers	8270 8250	8110	
Nitroaromatics and Cyclic Ketones	8270 8250	8090	
Nitrosoamines	8270 8250	8070	
Organochlorine Pesticides and PCBs	8270*	8080 8081	
Organophosphorous Pesticides	8270*	8140 8141	8321
Phenols	8270 8250	8040	
Phthalate Esters	8270 8250	8060 8061	
Polynuclear Hydrocarbons	8270 8250	8100	8310
VOLATILES			
Acrolein, Acrylonitrile, or Acetonitrile	8240	8030 8031	8316 8315
Acrylamide		8032	8316
Aromatic Volatiles	8240 8260	8020 8021	
Formaldehyde			8315
Halogenated Volatiles	8240 8260	8010 8011 8021	
Non-halogenated Volatiles	8240	8015	
Volatile Organics	8240 8260	8021	

*This method is an alternative confirmation method. It is not the method of choice.

FIGURE 2-1.
ORGANIC ANALYSIS OPTIONS

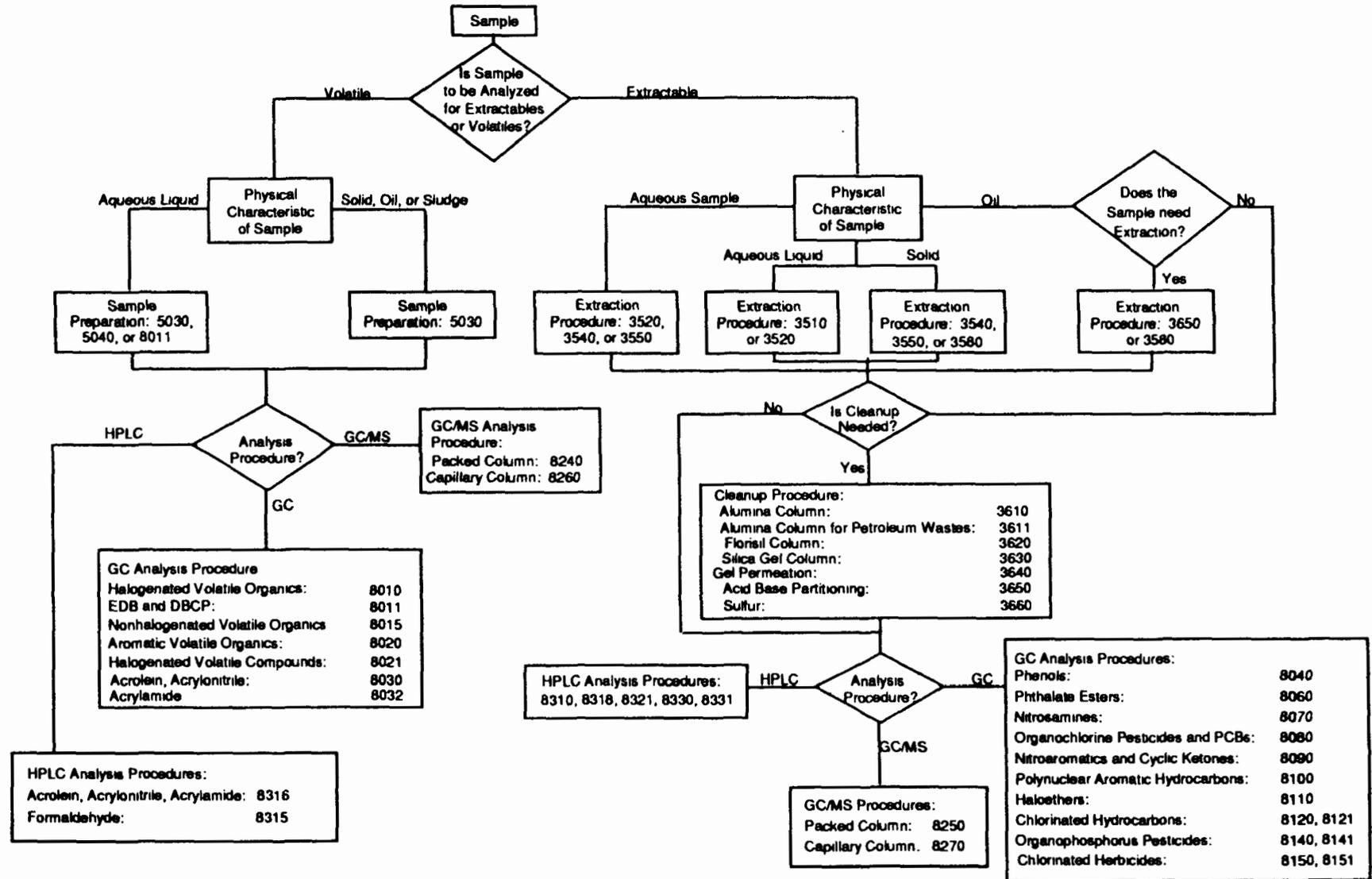


FIGURE 2-2.
SCHEMATIC OF SEQUENCE TO DETERMINE
IF A WASTE IS HAZARDOUS BY CHARACTERISTIC

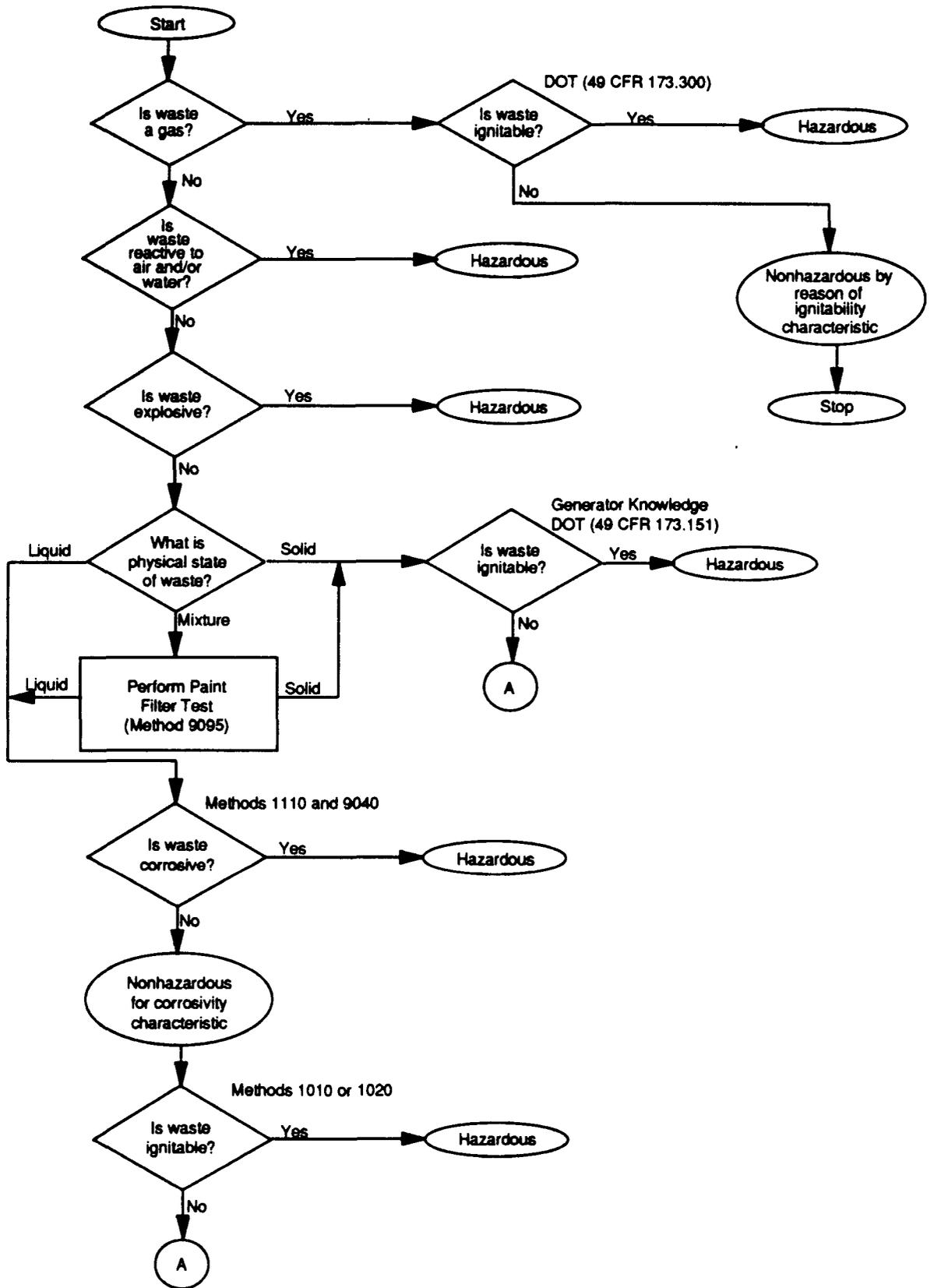


FIGURE 2-2.
(Continued)

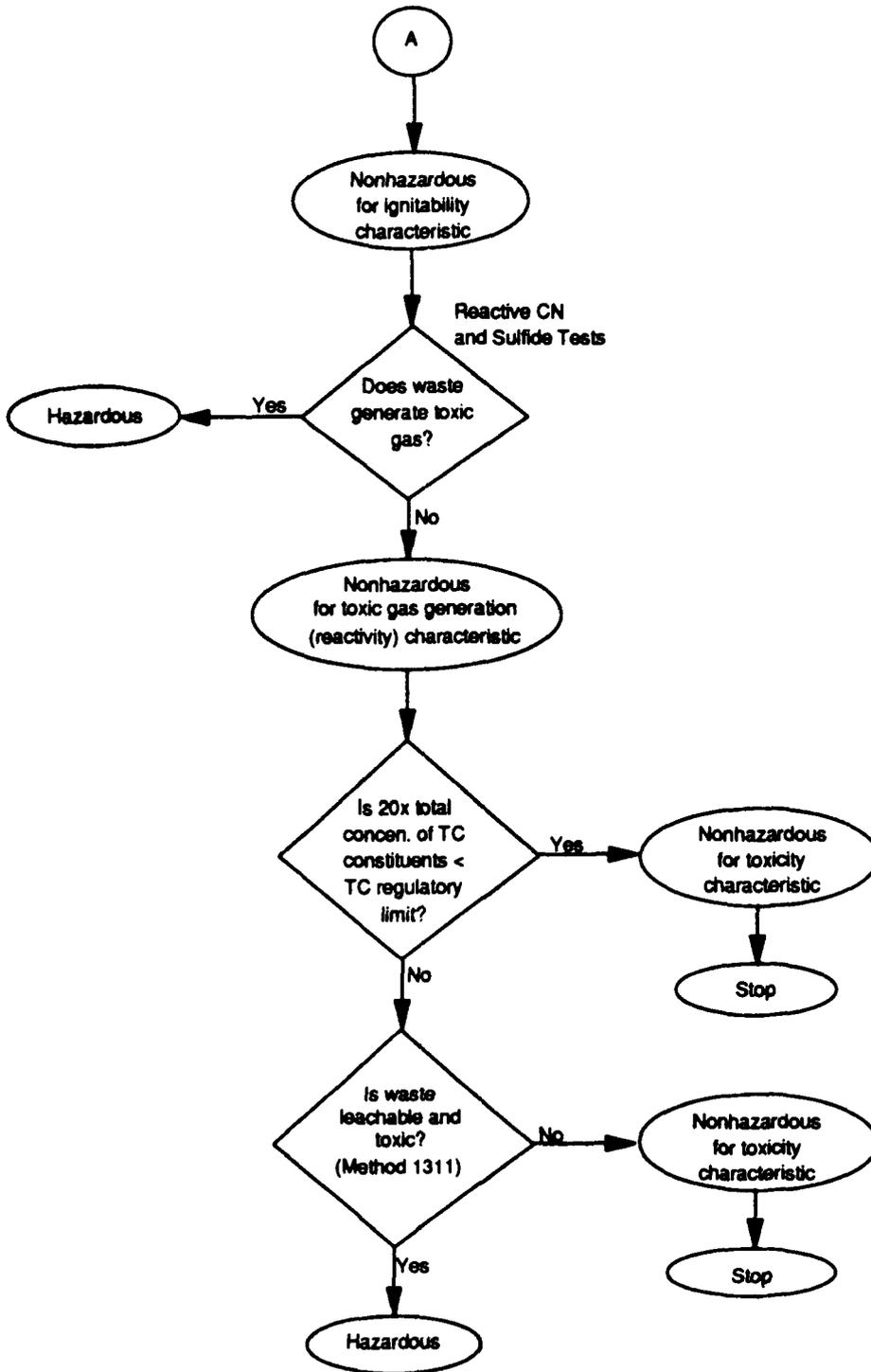


FIGURE 2-3A.
EP

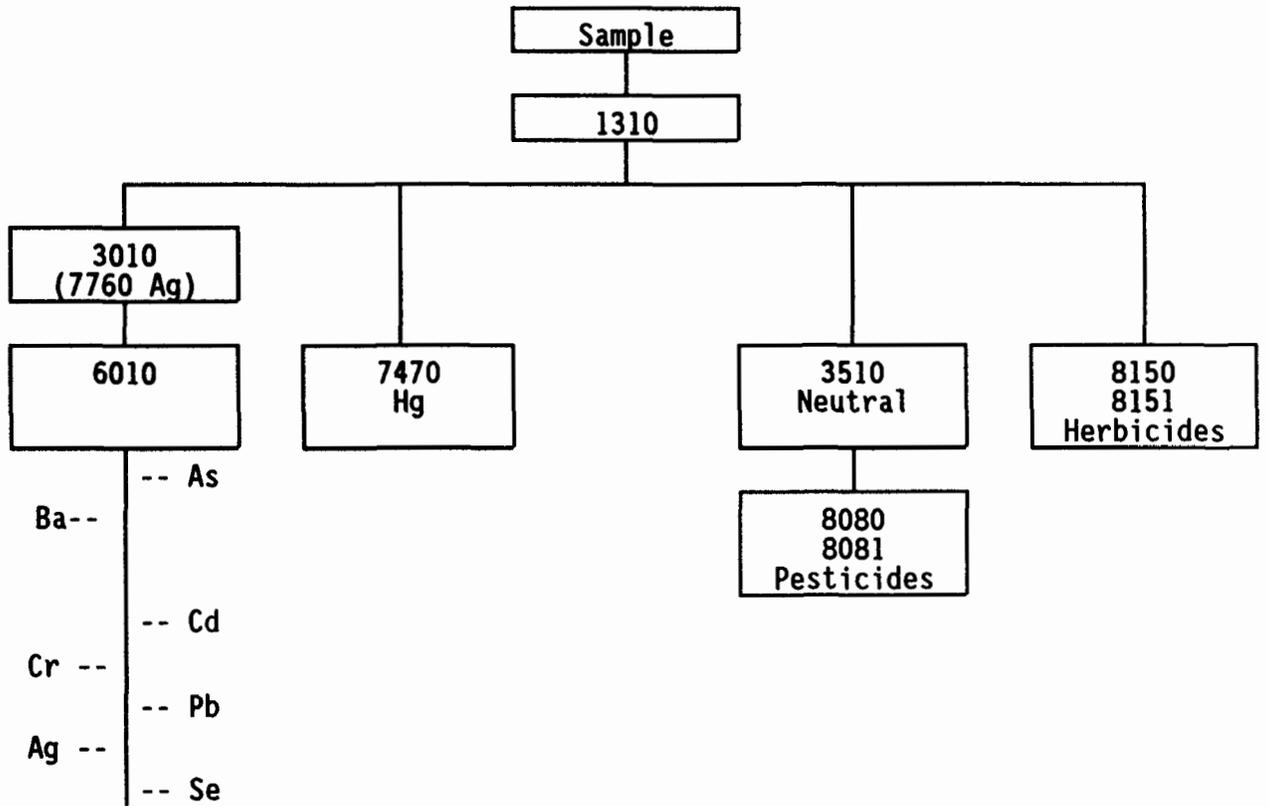


FIGURE 2-3B.
 RECOMMENDED SW-846 METHODS OF ANALYSIS FOR TCLP LEACHATES

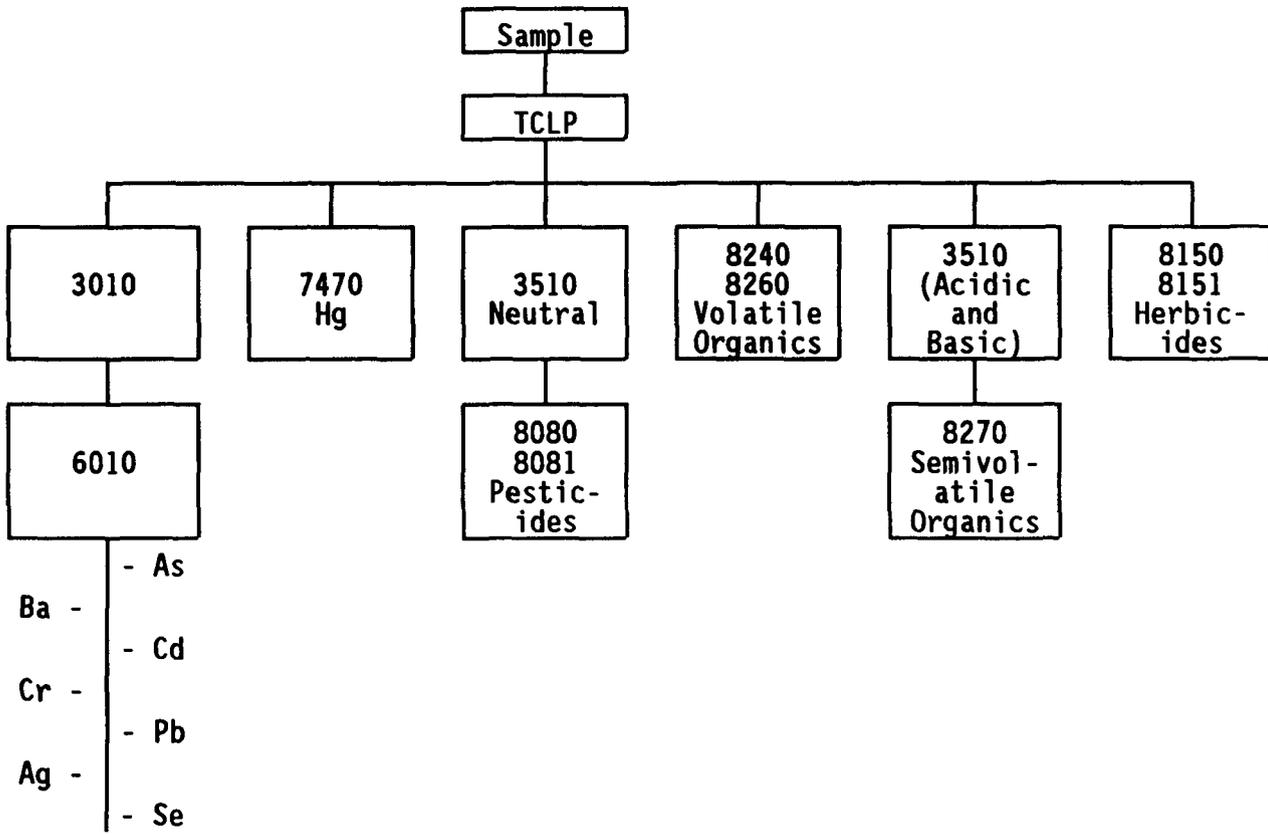
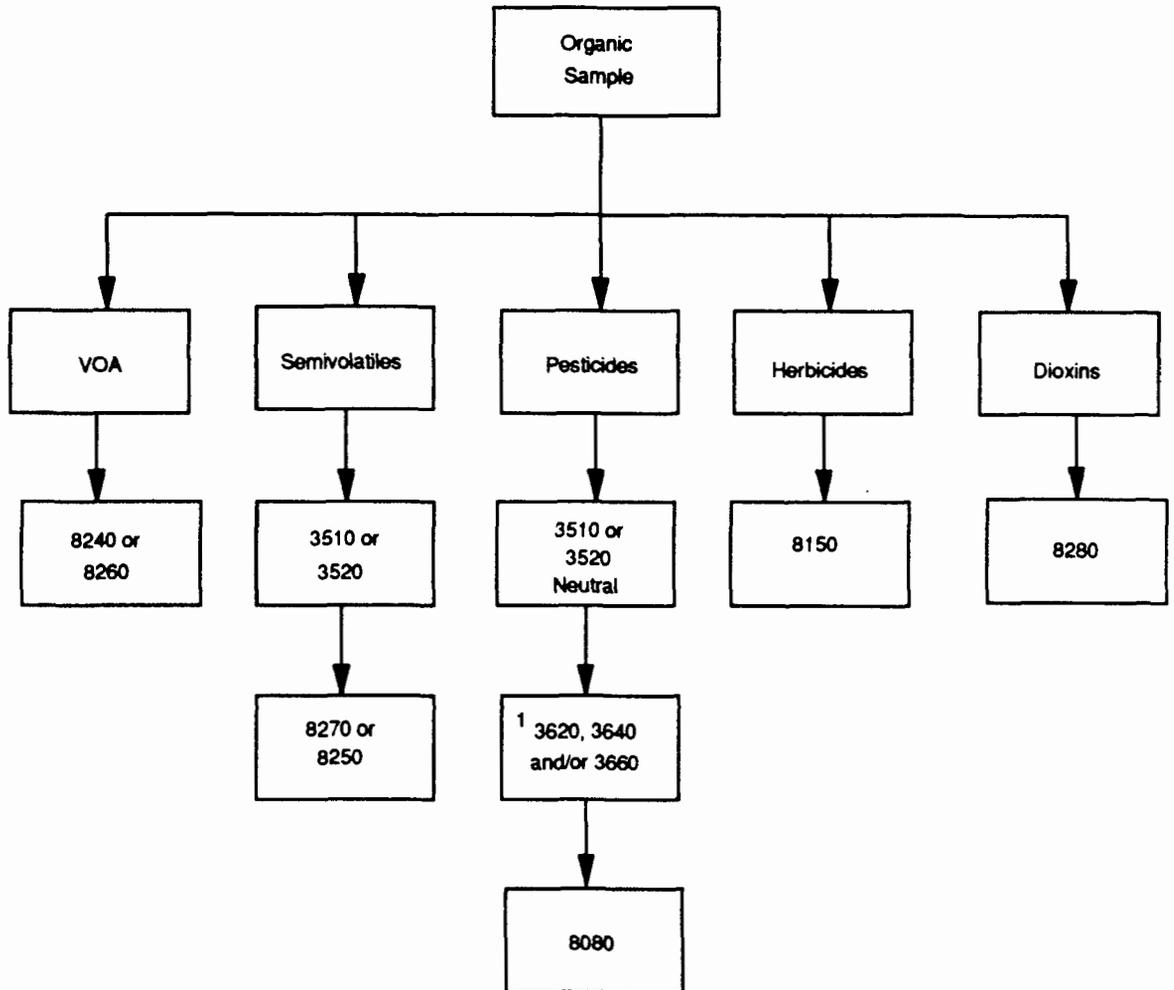
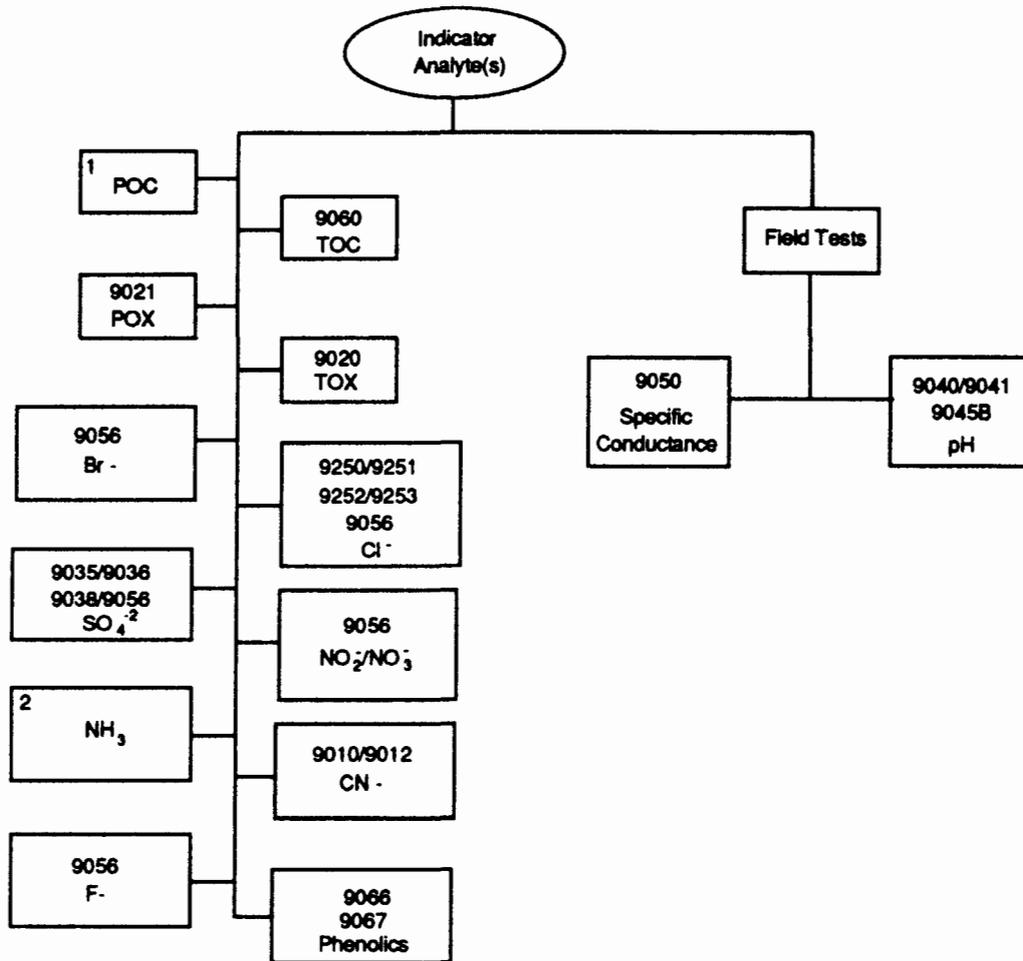


FIGURE 2-4A.
GROUND WATER ANALYSIS



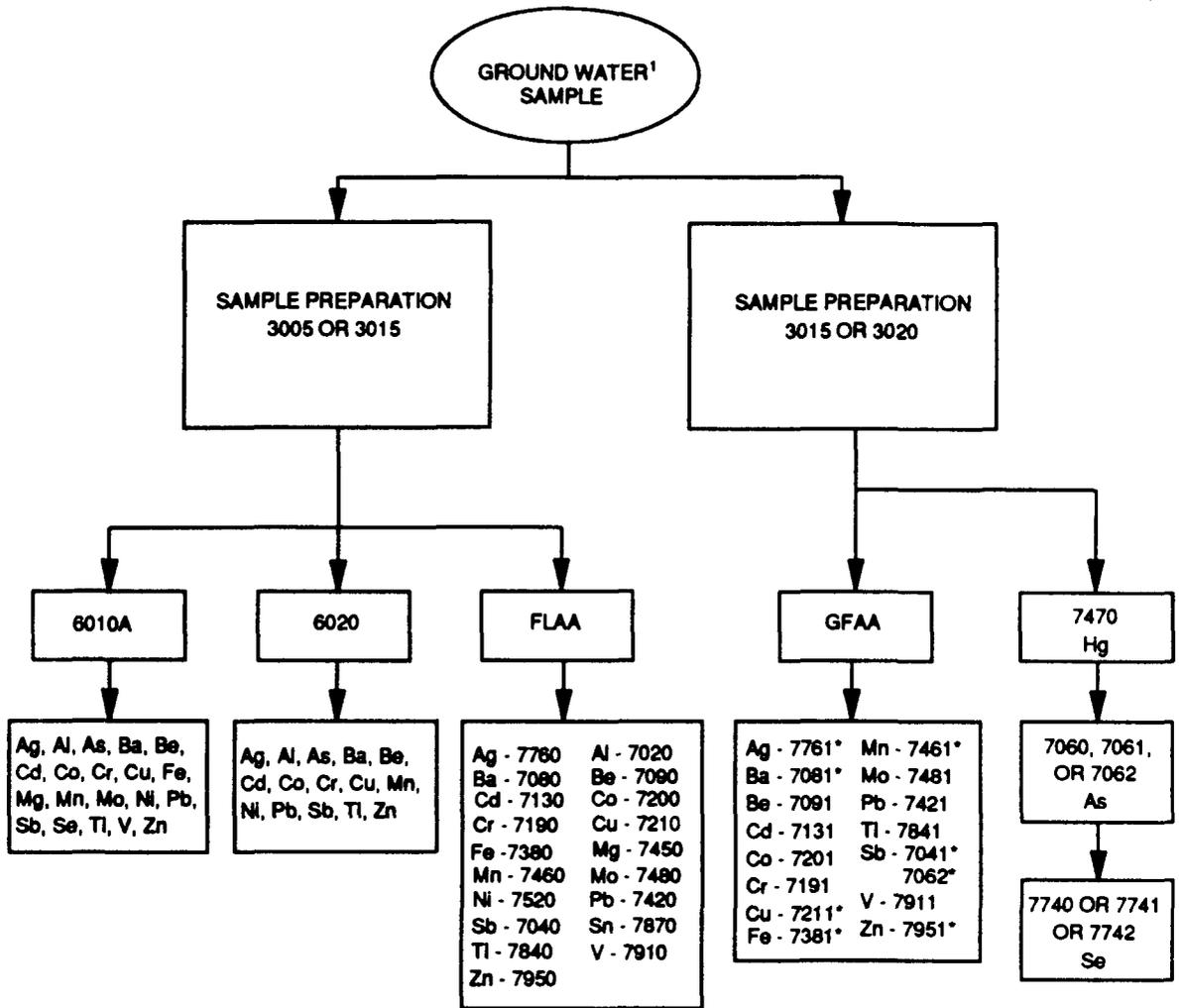
1 - Optional: Cleanup required only if interferences prevent analysis

FIGURE 2-4B.
INDICATOR ANALYTE



1 - Barcelona, 1984, (See Reference 1)
2 - Riggan, 1984, (See Reference 2)

FIGURE 2-4C.
GROUND WATER



* Follow the digestion procedures as detailed in the individual determinative methods.

¹ When analyzing for total dissolved metals, digestion is not necessary if the samples are filtered at the time of collection, and then acidified to the same concentration as the standards.

CHAPTER THREE

METALLIC ANALYTES

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of metals in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific metal components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

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 conditions employed.

Sensitivity: a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in sample after the sample is filtered through a 0.45-um filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-um filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050 or 3051.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

Initial calibration verification standard (ICV): A certified (EPA or other) or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus several known amounts of standard. See Method 7000, Section 8.7 for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion procedures and suggested collection volumes are listed in Table 1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that required for the individual digestion procedures and recommended sample collection volumes.

In the determination of trace metals, 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) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water.

NOTE: Chromic acid should not be used to clean glassware, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

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

TABLE 3-1.

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION
VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Vol. Req. ^a (mL)	Collection Volume (mL) ^a	Treatment/ Preservative Holding Time ^c
<u>Metals</u> (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO ₃ to pH <2 6 months
Dissolved	100	600	Filter on site; HNO ₃ to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2g	200g	6 months
<u>Chromium VI:</u> ^b			
Aqueous	100	400	24 hr
Solid	---	200g	----
<u>Mercury:</u>			
Aqueous			
Total	100	400	HNO ₃ to pH <2 28 days
Dissolved	100	400	Filter; HNO ₃ to pH <2 28 days
Solid			
Total	0.2g	200g	28 days

^aUnless stated otherwise.

^bThe holding time for the analysis of hexavalent chromium in solid samples has not yet been determined. A holding time of "as soon as possible" is recommended.

^cAll samples must be stored at 4°C until analyzed, either glass or plastic containers may be used.

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.
2. "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.
3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986, p. 26660.
4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd edition, 1979.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metals determination by FLAA or ICP. The unfiltered or filtered sample is heated with dilute HCl and HNO₃ prior to metal determination.

Method 3010 prepares waste samples for total metal determination by FLAA and ICP. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total metal determination by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total metals determination by furnace GFAA. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3040 prepares oily waste samples for soluble metals determination by AA and ICP methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total metals determination by

AA and ICP. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051 prepares sludges, sediments, soils and oils for total metals determination by FLAA, GFAA, ICP-AES and ICP-MS. Nitric acid is added to the representative sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

3.3 METHODS FOR DETERMINATION OF METALS

This manual contains seven analytical techniques for trace metal determinations: inductively coupled argon plasma emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrometry (FLAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA or FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

CHAPTER FOUR
ORGANIC ANALYTES

4.1 GENERAL CONSIDERATIONS

4.1.1 Introduction

Following the initial and critical step of designing a sampling plan (Chapter Nine) is the implementation of that plan such that a representative sample of the solid waste is collected. Once the sample has been collected it must be stored and preserved to maintain the chemical and physical properties that it possessed at the time of collection. The sample type, type of containers and their preparation, possible forms of contamination, and preservation methods are all items which must be thoroughly examined in order to maintain the integrity of the samples. This section highlights considerations which must be addressed in order to maintain a sample's integrity and representativeness. This section is, however, applicable only to trace analyses.

Quality Control requirements need not be met for all compounds presented in the Table of Analytes for the method in use, rather, they must be met for all compounds reported. A report of non-detect is considered a quantitative report, and must meet all applicable QC requirements for that compound and the method used.

4.1.2 Sample Handling and Preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two and Table 4-1 of this section for sample containers, sample preservation, and sample holding time information.

Volatile Organics

Standard 40 mL glass screw-cap VOA vials with Teflon lined silicone septa may be used for both liquid and solid matrices. The vials and septa should be washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100°C for approximately one hour.

NOTE: Do not heat the septa for extended periods of time (i.e. more than one hour, because the silicone begins to slowly degrade at 105°C).

When collecting the samples, liquids and solids should be introduced into the vials gently to reduce agitation which might drive off volatile compounds. In general, liquid samples should be poured into the vial without introducing any air bubbles within the vial as it is being filled. Should bubbling occur as a result of violent pouring, the sample must be poured out and the vial refilled. The vials should be completely filled at the time of sampling, so that when the septum cap is fitted and sealed, and the vial inverted, no headspace is visible. The sample should be hermetically sealed in the vial at the time of sampling, and must not be opened prior to analysis to preserve their integrity.

- due to differing solubility and diffusion properties of gases in LIQUID matrices at different temperatures, it is possible for the sample to generate some headspace during storage. This headspace will appear in the form of micro bubbles, and should not invalidate a sample for volatiles analysis.
- The presence of a macro bubble in a sample vial generally indicates either improper sampling technique or a source of gas evolution within the sample. The latter case is usually accompanied by a buildup of pressure within the vial, (e.g. carbonate-containing samples preserved with acid). Studies conducted by the USEPA (EMSL-Ci, unpublished data) indicate that "pea-sized" bubbles (i.e. bubbles not exceeding 1/4 inch or 6 mm in diameter) did not adversely affect volatiles data. These bubbles were generally encountered in wastewater samples, which are more susceptible to variations in gas solubility than are groundwater samples.

At the time of analysis, the aliquot to be analyzed should be taken from the vial with a gas-tight syringe inserted directly through the septum of the vial. Only one analytical sample can be taken from each vial. If these guidelines are not followed, the validity of the data generated from the samples is suspect.

VOA vials for samples with solid or semi-solid matrices (e.g., sludges) should be completely filled as best as possible. The vials should be tapped slightly as they are filled to try and eliminate as much free air space as possible. Two vials should also be filled per sample location.

At least two VOA vials should be filled and labeled immediately at the point at which the sample is collected. They should NOT be filled near a running motor or any type of exhaust system because discharged fumes and vapors may contaminate the samples. The two vials from each sampling location should then be sealed in separate plastic bags to prevent cross-contamination between samples, particularly if the sampled waste is suspected of containing high levels of volatile organics. (Activated carbon may also be included in the bags to prevent cross-contamination from highly contaminated samples). VOA samples may also be contaminated by diffusion of volatile organics through the septum during shipment and storage. To monitor possible contamination, a trip blank prepared from organic-free reagent water (as defined in Chapter One) should be carried throughout the sampling, storage, and shipping process.

Semivolatile Organics (including Pesticides, PCBs and Herbicides.)

Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing (see Section 4.1.4 for specific instructions on glassware cleaning). The sample containers should be of glass or Teflon, and have screw-caps with Teflon lined septa. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. However, acidic or basic samples may react with the aluminum foil, causing eventual contamination of the sample. Plastic containers or lids may NOT be used for the storage of samples due to the possibility of sample contamination from the phthalate esters and other hydrocarbons within the plastic. Sample containers should be filled with care so as to prevent any portion of the collected sample coming in contact with the sampler's gloves, thus causing contamination. Samples should not be

collected or stored in the presence of exhaust fumes. If the sample comes in contact with the sampler (e.g. if an automatic sampler is used), run organic-free reagent water through the sampler and use as a field blank.

4.1.3 Safety

Safety should always be the primary consideration in the collection of samples. A thorough understanding of the waste production process, as well as all of the potential hazards making up the waste, should be investigated whenever possible. The site should be visually evaluated just prior to sampling to determine additional safety measures. Minimum protection of gloves and safety glasses should be worn to prevent sample contact with the skin and eyes. A respirator should be worn even when working outdoors if organic vapors are present. More hazardous sampling missions may require the use of supplied air and special clothing.

4.1.4 Cleaning of Glassware

In the analysis of samples containing components in the parts per billion range, the preparation of scrupulously clean glassware is mandatory. Failure to do so can lead to a myriad of problems in the interpretation of the final chromatograms due to the presence of extraneous peaks resulting from contamination. Particular care must be taken with glassware such as Soxhlet extractors, Kuderna-Danish evaporative concentrators, sampling-train components, or any other glassware coming in contact with an extract that will be evaporated to a smaller volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contaminating substance(s), which may seriously distort the results.

The basic cleaning steps are:

1. Removal of surface residuals immediately after use;
2. Hot soak to loosen and float most particulate material;
3. Hot water rinse to flush away floated particulates;
4. Soak with an oxidizing agent to destroy traces of organic compounds;
5. Hot water rinse to flush away materials loosened by the deep penetrant soak;
6. Distilled water rinse to remove metallic deposits from the tap water;
7. Alcohol, e.g., isopropanol or methanol, rinse to flush off any final traces of organic materials and remove the water; and
8. Flushing the item immediately before use with some of the same solvent that will be used in the analysis.

Each of these eight fundamental steps are discussed here in the order in which they appeared on the preceeding page.

1. As soon possible after glassware (i.e. beakers, pipets, flasks, or bottles) has come in contact with sample or standards, the glassware should be flushed with alcohol before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein.
2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard-water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard-water scum or curd would have an affinity particularly for many chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath in a thin film.

There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York, and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

3. No comments required.
4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of concentrated sulfuric acid and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40-50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with fluorocarbon sheeting because spattering will disintegrate any unprotected surfaces.

The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca. 0.1 N NaOH upon dilution, and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass or exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

- 5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware could pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended. It is recommended that laboratory glassware and equipment be dried at 100°C. Under no circumstances should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

As an alternate to solvent rinsing, the glassware can be heated to a minimum of 300°C to vaporize any organics. Do not use this high temperature treatment on volumetric glassware, glassware with ground glass joints, or sintered glassware.

4.1.5 High Concentration Samples

Cross contamination of trace concentration samples may occur when prepared in the same laboratory with high concentration samples. Ideally, if both type samples are being handled, a laboratory and glassware dedicated solely to the preparation of high concentration samples would be available for this purpose. If this is not feasible, as a minimum when preparing high concentration samples, disposable glassware should be used or, at least, glassware dedicated entirely to the high concentration samples. Avoid cleaning glassware used for both trace and high concentration samples in the same area.

TABLE 4-1.
 SAMPLE CONTAINERS, PRESERVATION, TECHNIQUES, AND HOLDING TIMES

Analyte Class	Container	Preservative	Holding Time
<u>Volatile Organics</u>			
Concentrated Waste Samples	125 mL widemouth glass container with Teflon lined lid	None	14 days
Liquid Samples			
No Residual Chlorine Present	2 X 40 mL vials with Teflon lined septum caps	Cool, 4°C ¹	14 days
Residual Chlorine Present	2 X 40 mL vials with Teflon lined septum caps	Collect sample in a 125 mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution. Gently swirl to mix sample and transfer to a 40 mL VOA vial. ¹ Cool, 4°C	14 days
Acrolein and Acrylonitrile	2 X 40 mL vials with Teflon lined septum caps	Adjust to pH 4-5; cool, 4°C	14 days
Soil/Sediments and Sludges	125 mL widemouth glass container sealed with a septum	Cool, 4°C	14 days

¹ Adjust pH <2 with H₂SO₄, HCl or solid NaHSO₄.

Analyte Class	Container	Preservative	Holding Time
Table 4-1 Continued			
<u>Semivolatile Organics/Organochlorine Pesticides/PCBs and Herbicides</u>			
Concentrated Waste Samples	125 mL widemouth glass with Teflon lined lid	None	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.
Water Samples			
No Residual Chlorine Present	1-gal. or 2 x 0.5-gal. amber glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Residual Chlorine Present	1-gal. or 2 x 0.5-gal. amber glass container with Teflon lined lid	Add 3 mL 10% sodium thiosulfate solution per gallon. ² Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days following extraction.
Soil/Sediments and Sludges	250 mL widemouth glass container with Teflon lined lid	Cool, 4°C	Samples must be extracted within 14 days and extracts analyzed within 40 days following extraction.

² Pre-preservation may be performed in the laboratory prior to field use.

4.2 SAMPLE PREPARATION METHODS

4.2.1 EXTRACTIONS AND PREPARATIONS

4.2 SAMPLE PREPARATION METHODS

4.2.2 CLEANUP

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.1 GAS CHROMATOGRAPHIC METHODS

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.2 GAS CHROMATOGRAPHIC/MASS SPECTROMETRIC METHODS

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.3 HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC METHODS

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.4 FOURIER TRANSFORM INFRARED METHODS

4.4. MISCELLANEOUS SCREENING METHODS

CHAPTER SEVEN

INTRODUCTION AND REGULATORY DEFINITIONS

7.1 IGNITABILITY

7.1.1 Introduction

This section discusses the hazardous characteristic of ignitability. The regulatory background of this characteristic is summarized, and the regulatory definition of ignitability is presented. The two testing methods associated with this characteristic, Methods 1010 and 1020, can be found in Chapter Eight.

The objective of the ignitability characteristic is to identify wastes that either present fire hazards under routine storage, disposal, and transportation or are capable of severely exacerbating a fire once started. Use the pressure filtration technique specified in Method 1311 (TCLP) to determine free liquid for the purpose of ignitability testing.

7.1.2 Regulatory Definition

The following definitions have been taken nearly verbatim from the RCRA regulations (40 CFR 261.21) and the DOT regulations (49 CFR §§ 173.300 and 173.151).

Characteristics Of Ignitability Regulation

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

1. It is a liquid, other than an aqueous solution, containing < 24% alcohol by volume, and it has a flash point < 60°C (140°F), as determined by a Pensky-Martens Closed Cup Tester, using the test method specified in ASTM Standard D-93-79 or D-93-80, 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 Sections 260.20 and 260.21. (ASTM standards are available from ASTM, 1916 Race Street, Philadelphia, PA 19103.)
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 by equivalent test methods approved by the Administrator under Sections 260.20 and 260.21.
4. It is an oxidizer, as defined in 49 CFR 173.151.

Ignitable Compressed Gas

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

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

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

Oxidizer

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

7.2 CORROSIVITY

7.2.1 Introduction

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

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

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

The following sections present the regulatory background and the regulation pertaining to the definition of corrosivity. The procedures for measuring pH of aqueous wastes are detailed in Method 9040, Chapter Six. Method 1110, Chapter Eight, describes how to determine whether a waste is corrosive to steel. Use the pressure filtration technique specified in Method 1311 (TCLP) to determine free liquid.

7.2.2 Regulatory Definition

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

1. A solid waste exhibits the characteristic of corrosivity if a representative sample of the waste has either of the following properties:
 - a. It is aqueous and has a pH ≤ 2 or ≥ 12.5 , as determined by a pH meter using either the test method specified in this manual (Method 9040) or an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.
 - b. It is a liquid and corrodes steel (SAE 1020) at rate > 6.35 mm (0.250 in.) per year at a test temperature of 55°C (130°F), as determined by the test method specified in NACE (National Association of Corrosion Engineers) Standard TM-01-69, as standardized in this manual (Method 1110) or an equivalent test method approved by the Administrator under the procedures set forth in Sections 260.20 and 260.21.

7.3 REACTIVITY

7.3.1 Introduction

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

This definition is intended to identify wastes that, 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 almost entirely on a descriptive, prose definition of reactivity because most of the available tests for measuring the variegated class of effects embraced by the reactivity definition suffer from a number of deficiencies.

7.3.2 Regulatory Definition

7.3.2.1 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. (Interim Guidance for Reactive Cyanide and Reactive Sulfide, Steps 7.3.3 and 7.3.4 below, can be used to detect the presence of reactive cyanide and reactive sulfide in wastes.)
6. It is capable of detonation or explosive reaction if it is subjected to a strong initiating source or if heated under confinement.

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.

7.3.3 Interim Guidance For Reactive Cyanide

7.3.3.1 The current EPA guidance level is:

Total releasable cyanide: 250 mg HCN/kg waste.

7.3.3.2 Test Method to Determine Hydrogen Cyanide Released from Wastes

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that wastes that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrocyanic acid upon contact with an aqueous acid.

1.3 This test measures only the hydrocyanic acid evolved at the test conditions. It is not intended to measure forms of cyanide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the cyanide is Method 9010, Chapter Five, starting with Step 7.2.7 of that method.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 1)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sulfuric acid (0.01N), H_2SO_4 . Add 2.8 mL concentrated H_2SO_4 to reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the 0.01N H_2SO_4 .

5.4 Cyanide reference solution, (1000 mg/L). Dissolve approximately 2.5 g of KOH and 2.51 g of KCN in 1 liter of reagent water. Standardize with 0.0192N $AgNO_3$. Cyanide concentration in this solution should be 1 mg/mL.

5.5 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 liter with reagent water.

5.7 Silver nitrate solution (0.0192N). Prepare by crushing approximately 5 g of $AgNO_3$ crystals and drying to constant weight at 40°C. Weigh 3.265 g of dried $AgNO_3$, dissolve in reagent water, and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide or a combination of sulfide and cyanide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of cyanide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base, this will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical

characteristics of the waste which may affect the rate of release of the hydrocyanic acid. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution (Step 5.6) to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

7.2 Close the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system.

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full. Start the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of cyanide in the scrubber by Method 9010, Chapter Five, starting with Step 7.2.7 of the method.

NOTE: Delete the "C" and "D" terms from the spectrophotometric procedure calculation and the "E" and "F" terms from the titration procedure calculation in Method 9010. These terms are not necessary for the reactivity determination because the terms determine the amount of cyanide in the entire sample, rather than only in the aliquot taken for analysis.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of HCN, using the following parameters:

X = Concentration of HCN in diluted scrubber solution (mg/L)
(This is obtained from Method 9010.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of measurement (sec.) = Time N₂ stopped - Time N₂ started

R = specific rate of release (mg/kg/sec.) = $\frac{X \cdot L}{W \cdot S}$

Total releasable HCN (mg/kg) = R x S

9.0 METHOD PERFORMANCE

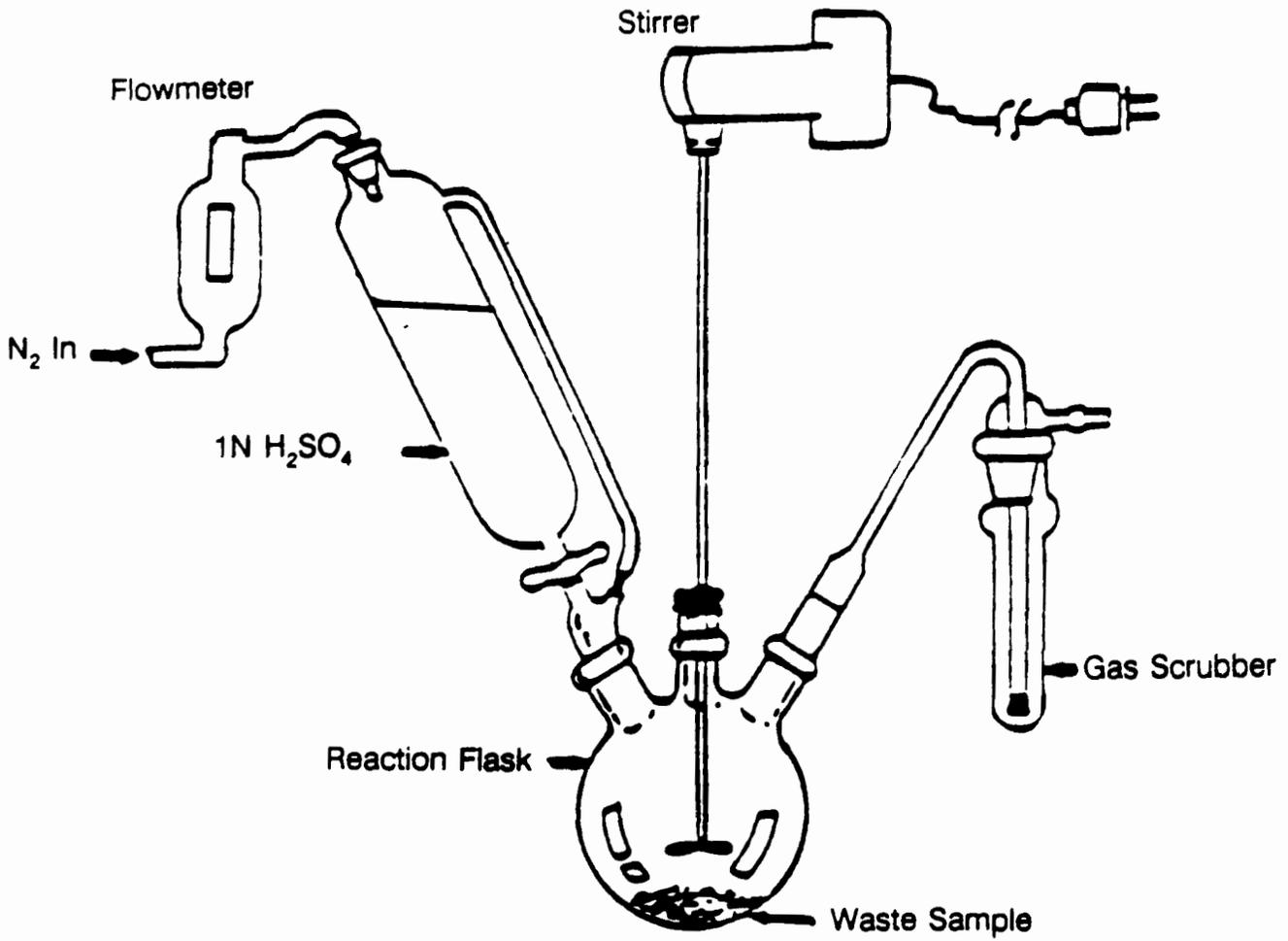
9.1 The operation of the system can be checked and verified using the cyanide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 1.

APPARATUS TO DETERMINE HYDROGEN CYANIDE RELEASED FROM WASTES



7.3.4 Interim Guidance For Reactive Sulfide

7.3.4.1 The current EPA guidance level is:

Total releasable sulfide: 500 mg H₂S/kg waste.

7.3.4.2 Test Method to Determine Hydrogen Sulfide Released from Wastes

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to all wastes, with the condition that waste that are combined with acids do not form explosive mixtures.

1.2 This method provides a way to determine the specific rate of release of hydrogen sulfide upon contact with an aqueous acid.

1.3 This procedure releases only the hydrogen sulfide evolved at the test conditions. It is not intended to measure forms of sulfide other than those that are evolvable under the test conditions.

2.0 SUMMARY OF METHOD

2.1 An aliquot of acid is added to a fixed weight of waste in a closed system. The generated gas is swept into a scrubber. The analyte is quantified. The procedure for quantifying the sulfide is given in Method 9030, Chapter Five, starting with Step 7.3 of that method.

3.0 INTERFERENCES

3.1 Interferences are undetermined.

4.0 APPARATUS AND MATERIALS (See Figure 2)

4.1 Round-bottom flask - 500-mL, three-neck, with 24/40 ground-glass joints.

4.2 Gas scrubber - 50 mL calibrated scrubber.

4.3 Stirring apparatus - To achieve approximately 30 rpm. This may be either a rotating magnet and stirring bar combination or an overhead motor-driven propeller stirrer.

4.4 Addition funnel - With pressure-equalizing tube and 24/40 ground-glass joint and Teflon sleeve.

4.5 Flexible tubing - For connection from nitrogen supply to apparatus.

4.6 Water-pumped or oil-pumped nitrogen gas - With two-stage regulator.

4.7 Rotometer - For monitoring nitrogen gas flow rate.

4.8 Analytical balance - capable of weighing to 0.001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sulfuric acid (0.01N), H_2SO_4 . Add 2.8 mL concentrated H_2SO_4 to reagent water and dilute to 1 L. Withdraw 100 mL of this solution and dilute to 1 L to make the 0.01N H_2SO_4 .

5.4 Sulfide reference solution - Dissolve 4.02 g of $Na_2S \cdot 9H_2O$ in 1.0 liter of reagent water. This solution contains 570 mg/L hydrogen sulfide. Dilute this stock solution to cover the analytical range required (100-570 mg/L).

5.5 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in reagent water and dilute to 1 liter with reagent water.

5.6 Sodium hydroxide solution (0.25N), NaOH. Dilute 200 mL of 1.25N sodium hydroxide solution (Step 5.5) to 1 liter with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 Samples containing, or suspected of containing, sulfide wastes should be collected with a minimum of aeration. The sample bottle should be filled completely, excluding all head space, and stoppered. Analysis should commence as soon as possible, and samples should be kept in a cool, dark place until analysis begins.

6.2 It is suggested that samples of sulfide wastes be tested as quickly as possible. Although they can be preserved by adjusting the sample pH to 12 with strong base and adding zinc acetate to the sample, these will cause dilution of the sample, increase the ionic strength, and, possibly, change other physical or chemical characteristics of the waste which may affect the rate of release of the hydrogen sulfide. Storage of samples should be under refrigeration and in the dark.

6.3 Testing should be performed in a ventilated hood.

7.0 PROCEDURE

7.1 Add 50 mL of 0.25N NaOH solution to a calibrated scrubber and dilute with reagent water to obtain an adequate depth of liquid.

7.2 Assemble the system and adjust the flow rate of nitrogen, using the rotometer. Flow should be 60 mL/min.

7.3 Add 10 g of the waste to be tested to the system .

7.4 With the nitrogen flowing, add enough sulfuric acid to fill the flask half full, while starting the 30 minute test period.

7.5 Begin stirring while the acid is entering the round-bottom flask. The stirring speed must remain constant throughout the test.

NOTE: The stirring should not be fast enough to create a vortex.

7.6 After 30 minutes, close off the nitrogen and disconnect the scrubber. Determine the amount of sulfide in the scrubber by Method 9030, Chapter Five, starting with Step 7.3 of that method.

7.7 Substitute the following for Step 7.3.2 in Method 9030: The trapping solution must be brought to a pH of 2 before proceeding. Titrate a small aliquot of the trapping solution to a pH 2 end point with 6N HCl and calculate the amount of HCl needed to acidify the entire scrubber solution. Combine the small acidified aliquot with the remainder of the acidified scrubber solution.

8.0 CALCULATIONS

8.1 Determine the specific rate of release of H₂S, using the following parameters:

X = Concentration of H₂S in scrubber (mg/L)
(This is obtained from Method 9030.)

L = Volume of solution in scrubber (L)

W = Weight of waste used (kg)

S = Time of experiment (sec.) = Time N₂ stopped - Time N₂ started

R = specific rate of release (mg/kg/sec.) = $\frac{X \cdot L}{W \cdot S}$

Total releasable H₂S (mg/kg) = R x S

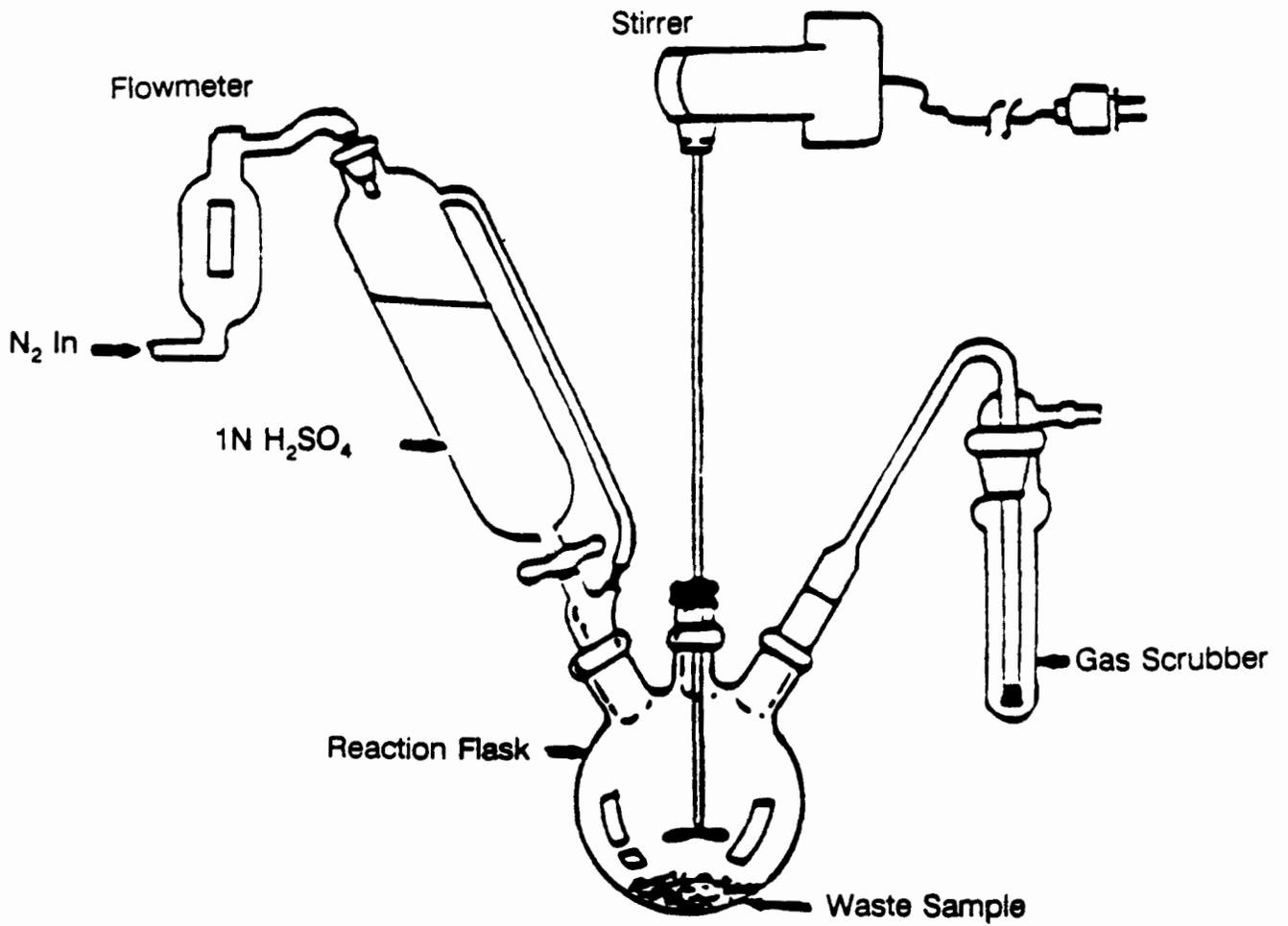
9.0 METHOD PERFORMANCE

9.1 The operation of the system can be checked and verified using the sulfide reference solution (Step 5.4). Perform the procedure using the reference solution as a sample and determine the percent recovery. Evaluate the standard recovery based on historical laboratory data, as stated in Chapter One.

10.0 REFERENCES

10.1 No references are available at this time.

FIGURE 2.
APPARATUS TO DETERMINE HYDROGEN SULFIDE RELEASED FROM WASTES



7.4 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

7.4.1 Introduction

The Toxicity Characteristic Leaching Procedure (TCLP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A subsample of a waste is extracted with the appropriate buffered acetic acid solution for 18 ± 2 hours. The extract obtained from the TCLP (the "TCLP extract") is then analyzed to determine if any of the thresholds established for the 40 Toxicity Characteristic (TC) constituents (listed in Table 7-1) have been exceeded or if the treatment standards established for the constituents listed in 40 CFR §268.41 have been met for the Land Disposal Restrictions (LDR) program. If the TCLP extract contains any one of the TC constituents in an amount equal to or exceeding the concentrations specified in 40 CFR §261.24, the waste possesses the characteristic of toxicity and is a hazardous waste. If the TCLP extract contains LDR constituents in an amount exceeding the concentrations specified in 40 CFR §268.41, the treatment standard for that waste has not been met, and further treatment is necessary prior to land disposal.

7.4.2 Summary of Procedure

The TCLP consists of five steps (refer to Figure 3):

1. Separation Procedure

For liquid wastes (*i.e.*, those containing less than 0.5% dry solid material), the waste, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the TCLP extract.

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis.

2. Particle Size Reduction

Prior to extraction, the solid material must pass through a 9.5-mm (0.375-in.) standard sieve, have a surface area per gram of material equal to or greater than 3.1 cm^2 , or, be smaller than 1 cm in its narrowest dimension. If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to the surface area or particle size described above. (Special precautions must be taken if the solids are prepared for organic volatiles extraction.)

3. Extraction of Solid Material

The solid material from Step 2 is extracted for 18 ± 2 hours with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid

phase of the waste. A special extractor vessel is used when testing for volatile analytes.

4. Final Separation of the Extraction from the Remaining Solid

Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.8 μm glass fiber filter. If compatible, the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

5. Testing (Analysis) of TCLP Extract

Inorganic and organic species are identified and quantified using appropriate methods in the 6000, 7000, and 8000 series of methods in this manual or by equivalent methods.

7.4.3 Regulatory Definition

Under the Toxicity Characteristic, a solid waste exhibits the characteristic of toxicity if the TCLP extract from a subsample of the waste contains any of the contaminants listed in Table 7-1 at a concentration greater than or equal to the respective value given in that table. If a waste contains <0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

Under the Land Disposal Restrictions program, a restricted waste identified in 40 CFR §268.41 may be land disposed only if a TCLP extract of the waste or a TCLP extract of the treatment residue of the waste does not exceed the values shown in Table CCWE of 40 CFR §268.41 for any hazardous constituent listed in Table CCWE for that waste. If a waste contains <0.5% filterable solids, the waste itself, after filtering, is considered to be the extract for the purposes of analysis.

TABLE 7-1.

MAXIMUM CONCENTRATION OF CONTAMINANTS FOR TOXICITY CHARACTERISTIC

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0 ¹
m-Cresol	200.0 ¹
p-Cresol	200.0 ¹
Cresol	200.0 ¹
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13 ²
Endrin	0.02
Heptachlor (and its hydroxide)	0.008
Hexachlorobenzene	0.13 ²
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0 ²
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5

TABLE 7-1.

MAXIMUM CONCENTRATION OF CONTAMINANTS FOR TOXICITY CHARACTERISTIC

Contaminant	Regulatory Level (mg/L)
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

¹If o-, m-, and p-cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

²Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

FIGURE 3.

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE FLOWCHART

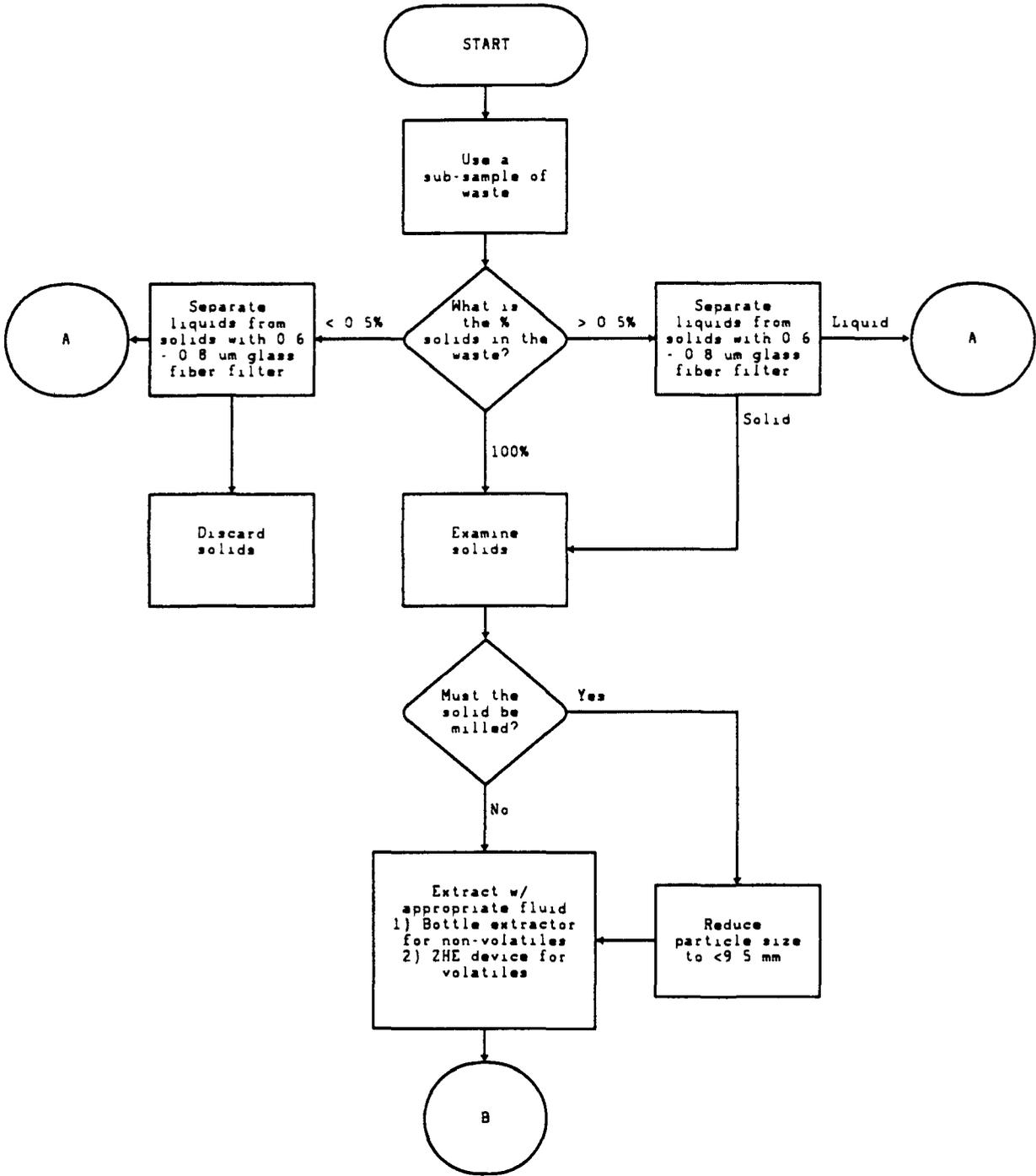
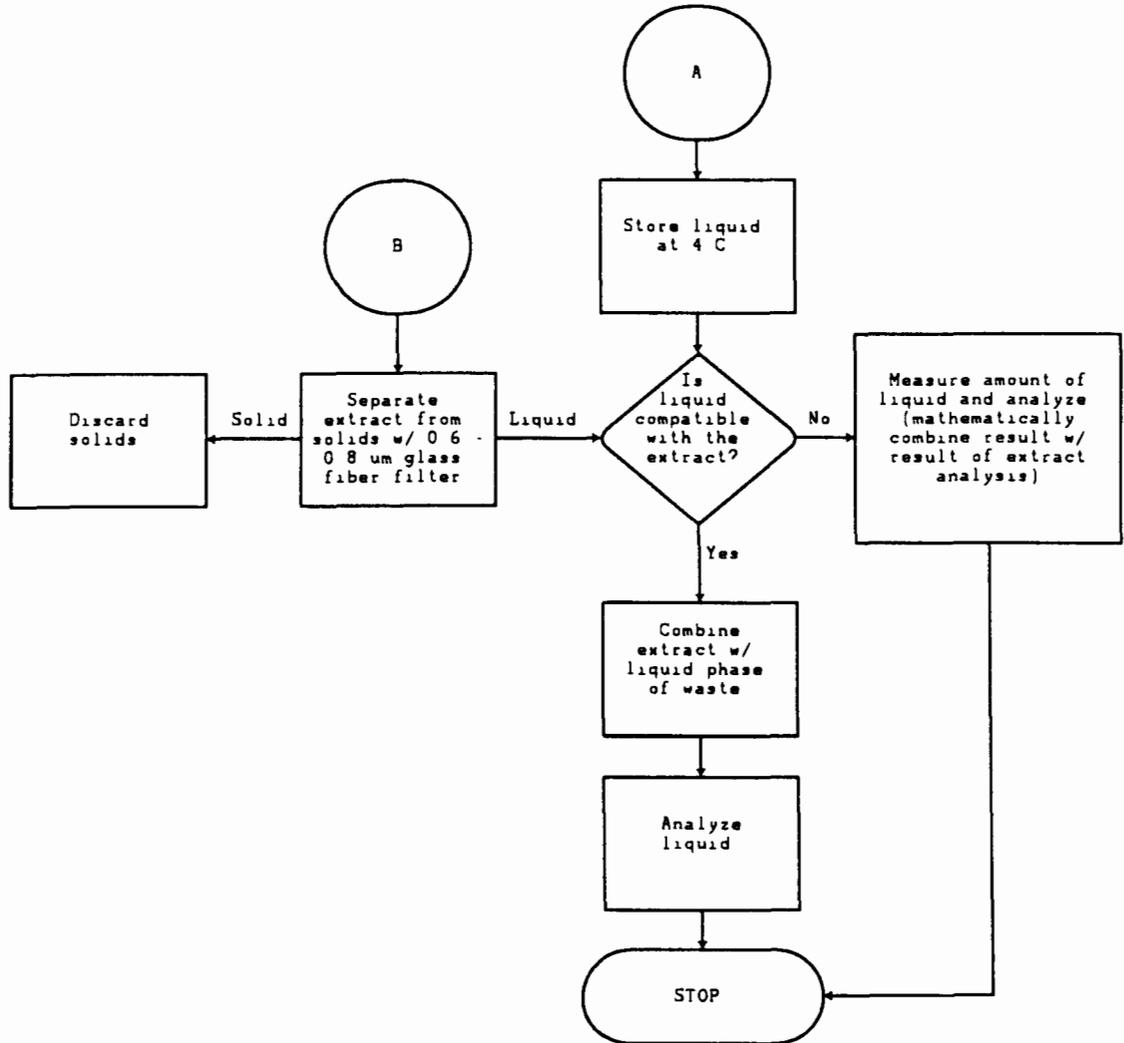


FIGURE 3.

TOXICITY CHARACTERISTIC LEACHATE PROCEDURE FLOWCHART



METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface water and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

*ICP only

**May be analyzed by ICP, FLAA, or GFAA

1.2 For the analysis of total dissolved metals, the sample is filtered at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.5-um filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is again filtered (if necessary) and diluted to volume and is then ready for analysis.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes.

4.2 Watch glasses.

4.3 Qualitative filter paper and filter funnels.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine level of impurities. If method blank is $<$ MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine level of impurities. If method blank is $<$ MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.5- μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed by FLAA or ICP, add 2 mL of concentrated HNO₃ and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a steam bath or hot plate at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO₃.

7.4 Adjust the final volume to 100 mL with water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks (calibration and reagent) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

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

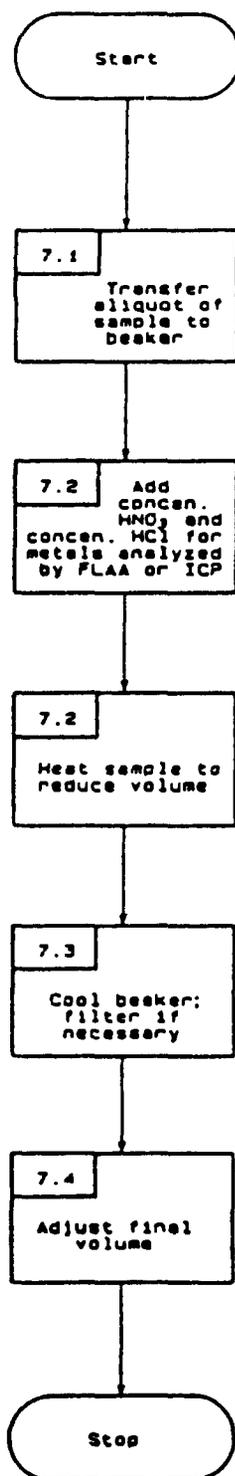
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3005
ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR
DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY



METHOD 3010

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for FLAA preparation for Silver.

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

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL.

4.2 Watch glasses - Ribbed and plain.

4.3 Quantitative filter paper or centrifugation equipment.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If method blank is $< \text{MDL}$, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl . Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is $< \text{MDL}$, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3 .

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

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3 . Cover the

beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO₃. Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks (calibration and reagent) should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater.

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

8.5 The method of standard addition shall be used for the analysis of all EP extracts (see Method 7000, Step 8.7).

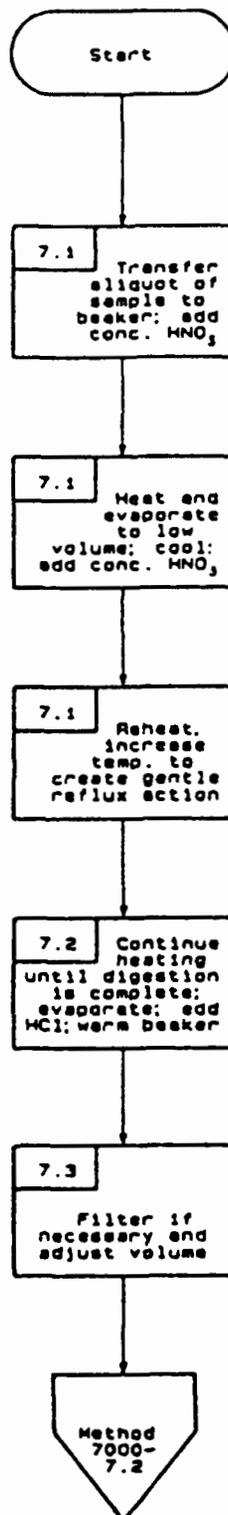
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3010
ACID DIGESTION PROCEDURE FOR FLAME ATOMIC ABSORPTION SPECTROSCOPY



METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
Zinc	

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 Nitric acid is added to an aqueous sample in a 120 mL Teflon digestion vessel. The vessel is capped and heated in a microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle in a clean sample bottle for analysis.

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. Samples that contain carbonates or other carbon dioxide generating compounds may cause enough pressure to vent the vessel. If this situation is anticipated the analyst may wish to use a smaller sample.

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires Teflon PFA digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

4.1.6 Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain Teflons may crack, burst, or explode in the oven under certain pressures. Only unlined PFA Teflon containers with pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

4.2 Plastic ware graduated cylinder, 50 or 100 mL capacity.

4.3 Quantitative filter paper, Whatman No. 41 or S&S White label or equivalent.

4.4 Analytical balance, 300 g capacity, minimum ± 0.01 g.

4.5 Disposable polypropylene filter funnel.

4.6 Polyethylene bottles, 125 mL, with caps

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated Nitric acid, HNO_3 . Acid should be analyzed to determine levels of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3 .

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water

exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97,95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ± 10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed ($1,000.0$ g \pm 0.1 g) into a Teflon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 3 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K) (C_p) (m) (\Delta T)}{t}$$

Eq. 1

P = the apparent power absorbed by the sample in watts (W).
(W=joule·sec⁻¹)

K = the conversion factor for thermochemical calories·sec⁻¹ to watts
(=4.184)

C_p = the heat capacity, thermal capacity, or specific heat
(cal·g⁻¹·°C⁻¹), of water

m = the mass of the water sample in grams (g),

ΔT = the final temperature minus the initial temperature (°C), and

t = the time in seconds (s).

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g⁻¹·°C⁻¹) the calibration equation simplifies to:

$$P = (\Delta T) (34.86) \quad \text{Eq. 2}$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid for a minimum of two hours followed with hot (1:1) nitric acid for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion

vessels is unknown or cross contamination from vessels is suspected. Polymeric volumetric ware and storage containers should be cleaned by leaching with more dilute acids appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

7.3 Sample Digestion

7.3.1 Weigh the Teflon PFA digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the Teflon digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft.lbs. (16-N m). Weigh each capped vessel to the nearest 0.01 g.

7.3.5 Place five vessels evenly distributed in the carousel. Blanks are treated as samples for the purpose of balancing the power input. When fewer than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Place the carousel in the unit; be sure to seat it carefully on the turntable. Program the microwave unit for the first-stage of the power program to give 545 W for 10 minutes and the second-stage program to give 344 W for 10 minutes. This sequence brings the samples to $160^{\circ}\text{C} \pm 4^{\circ}\text{C}$ in 10 minutes and permits a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units may be capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to $160^{\circ}\text{C} \pm 4^{\circ}\text{C}$ in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,2)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Rinse virgin or acid-cleaned polyethylene 125 mL bottles (or other suitable size) and caps with reagent water and shake out the large water drops. Label the bottles.

7.3.9 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.9.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.9.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.9.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

7.3.10 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a real sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

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

8.5 The method of standard addition shall be used for the analysis of all EP extracts (see Method 7000, Step 8.7).

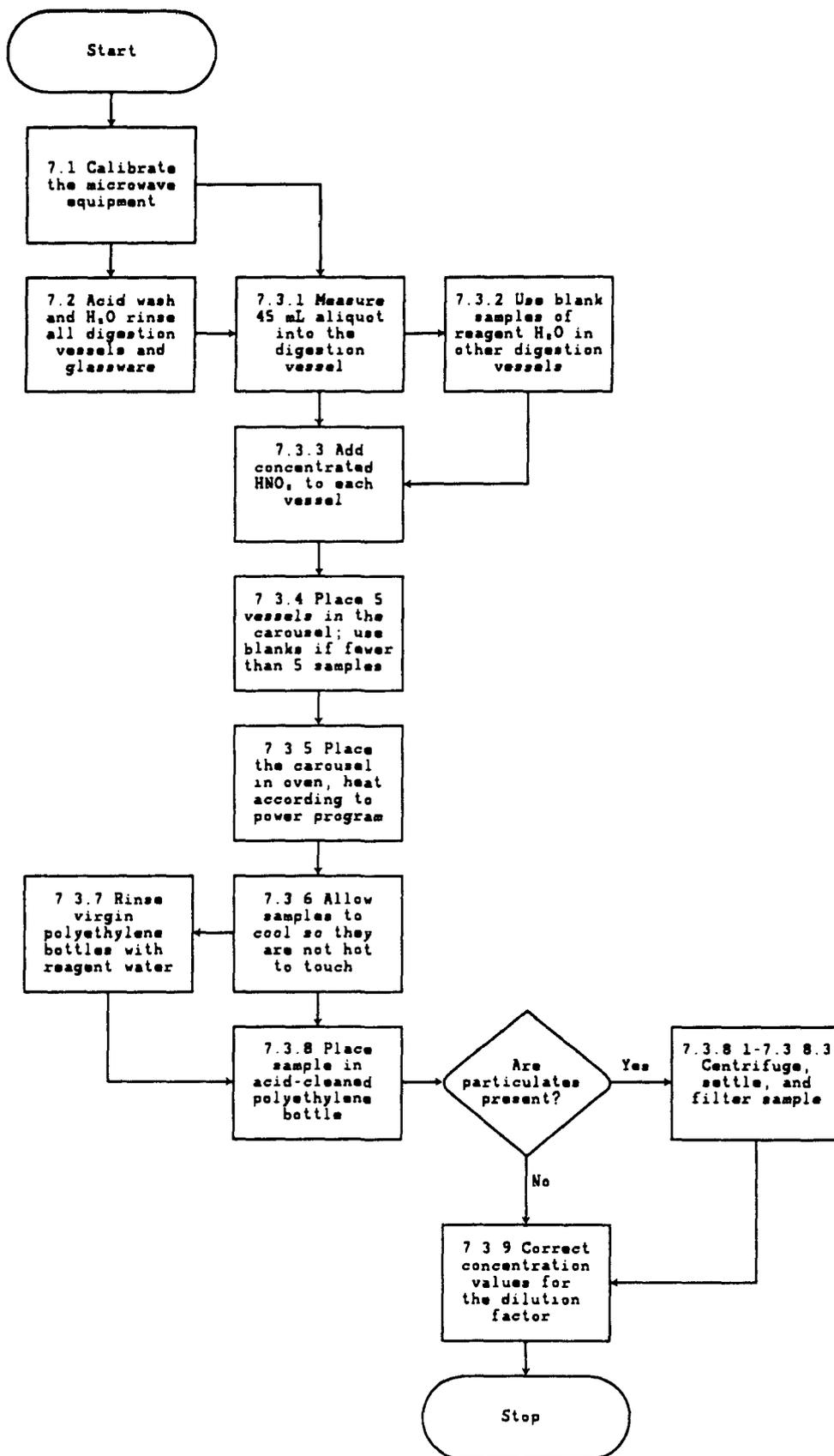
9.0 METHOD PERFORMANCE

9.1 Refer to Reference 4.

10.0 REFERENCES

1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M.; Jassie, L. B., Eds.; ACS Professional Reference Book Series: American Chemical Society, Washington, DC, 1988; Ch 6 & 11.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.
3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.
4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

METHOD 3015
MICROWAVE ASSISTED ACID DIGESTION
OF AQUEOUS SAMPLES AND EXTRACTS



METHOD 3020

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

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

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 7060 and 7740. For the digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL.

4.2 Watch glasses.

4.3 Qualitative filter paper or centrifugation equipment.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If method blank is $< \text{MDL}$, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3 .

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

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3 . Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO₃.) Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

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

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

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

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

8.6 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Step 8.7, for further information.

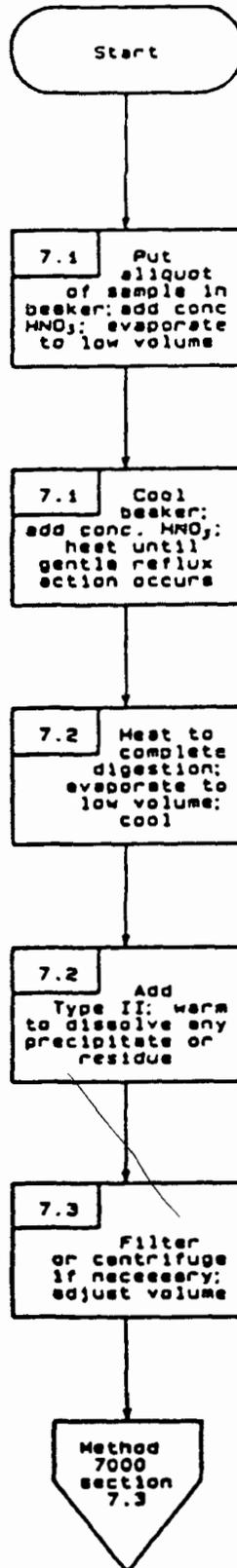
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3020
ACID DIGESTION FOR AQUEOUS SAMPLES AND EXTRACTS
FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY



METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

<u>FLAA</u>		<u>GFAA</u>
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Osmium	Cobalt
Chromium	Potassium	Iron
Cobalt	Silver	Lead
Copper	Sodium	Molybdenum
Iron	Thallium	Selenium
Lead	Vanadium	Thallium
	Zinc	Vanadium

NOTE: See Method 7760 for FLAA preparation for Silver.

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl, and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers - 250-mL.

- 4.2 Watch glasses.
- 4.3 Drying ovens - That can be maintained at 30°C.
- 4.4 Thermometer - That covers range of 0-200°C.
- 4.5 Filter paper - Whatman No. 41 or equivalent.
- 4.6 Centrifuge and centrifuge tubes.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrogen peroxide (30%), H_2O_2 . Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample.

7.2 Add 10 mL of 1:1 HNO₃, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO₃, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H₂O₂. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H₂O₂ in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H₂O₂.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to 100 mL with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with water.

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO₃. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with water.

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO₃. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

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

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

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

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

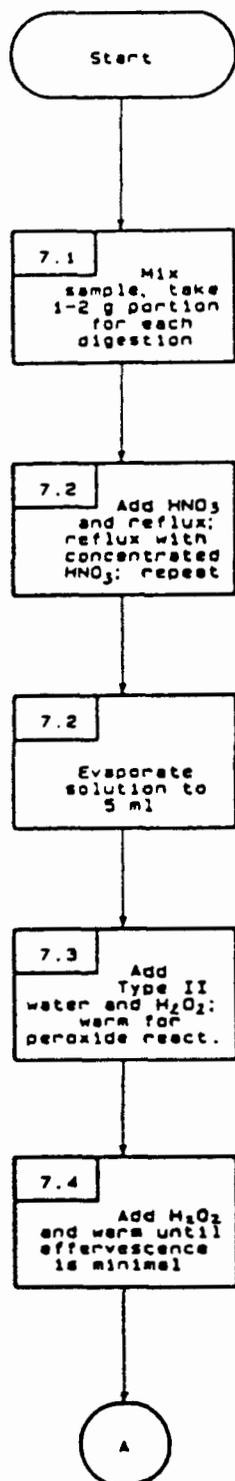
9.0 METHOD PERFORMANCE

9.1 No data provided.

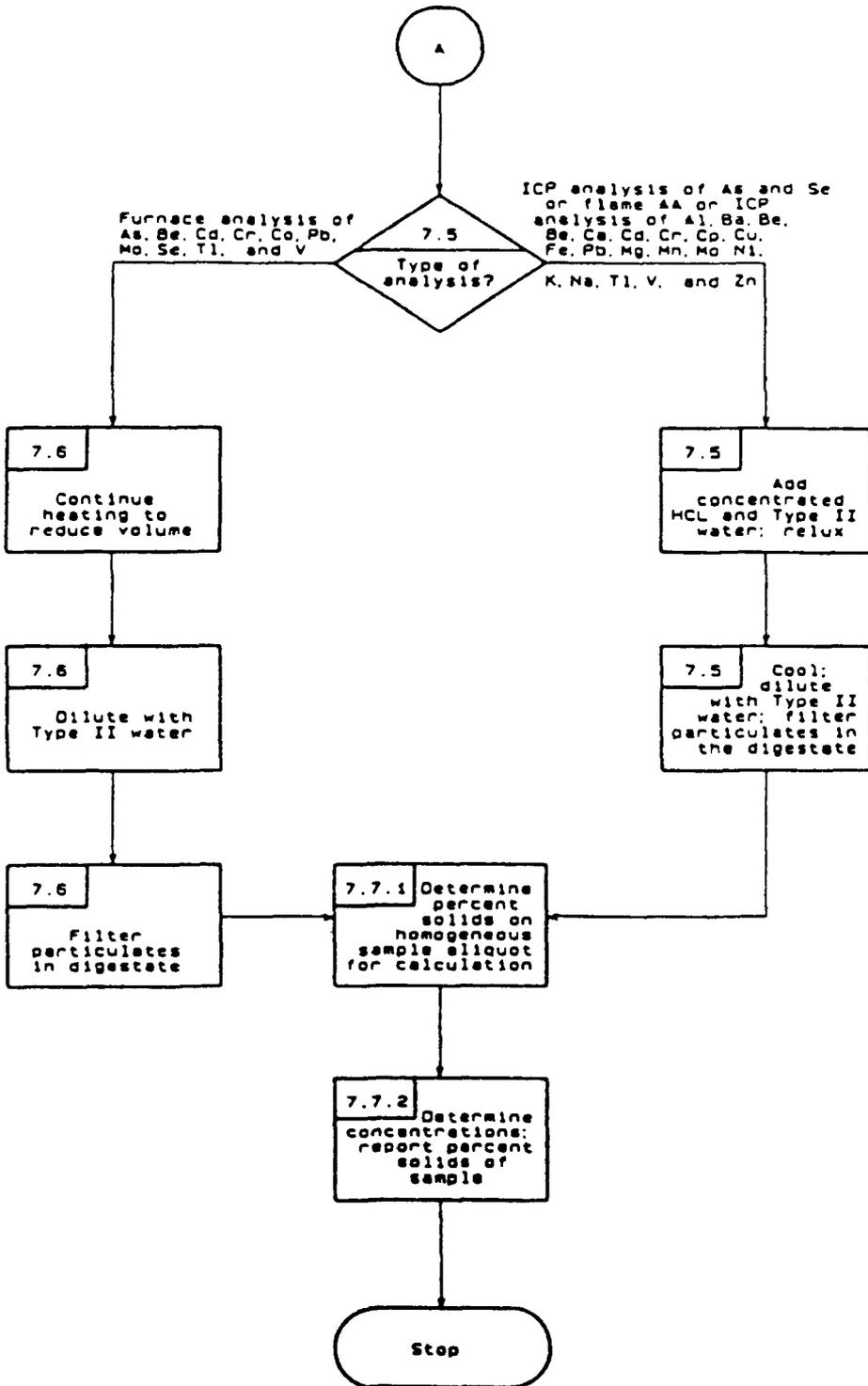
10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 3050
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS



METHOD 3050
ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS
(Continued)



METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS).

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample is placed in a Teflon PFA vessel with 10 mL of concentrated nitric acid. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5 ± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W and can be programmed to within ± 10 W of the required power.

4.1.2 The microwave unit cavity is corrosion resistant as well as ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires Teflon PFA digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

4.1.6 Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain Teflons may crack, burst, or explode in the unit under certain pressures. Only unlined PFA Teflon containers with pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

4.2 Polymeric volumetric ware in plastic (Teflon or polyethylene)
50 or 100 mL capacity.

- 4.3 Whatman No. 41 filter paper (or equivalent).
- 4.4 Disposable polypropylene filter funnel.
- 4.5 Analytical balance, 300 g capacity, and minimum ± 0.001 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

5.1.1 Concentrated nitric acid, HNO_3 . Acid should be analyzed to determine levels of impurity.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been

utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (± 10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ± 10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature ($23 \pm 2^\circ\text{C}$). One kg of reagent water is weighed ($1,000.0 \text{ g} \pm 0.1 \text{ g}$) into a Teflon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be $23 \pm 2^\circ\text{C}$ measured to $\pm 0.05^\circ\text{C}$. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to $\pm 0.05^\circ\text{C}$. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to $23 \pm 2^\circ\text{C}$. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$\text{Eq. 1} \quad P = \frac{(K) (C_p) (m) (\Delta T)}{t}$$

P = the apparent power absorbed by the sample in watts (W).
(W=joule·sec⁻¹)

K = the conversion factor for thermochemical calories·sec⁻¹ to watts
(=4.184)

C_p = the heat capacity, thermal capacity, or specific heat
(cal·g⁻¹·°C⁻¹), of water. m = the mass of the water sample in grams (g).

ΔT = the final temperature minus the initial temperature (°C), and

t = the time in seconds (s).

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g⁻¹·°C⁻¹) the calibration equation simplifies to:

$$\text{Eq. 2} \quad P = (\Delta T) (34.85)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid for a minimum of two hours followed with hot (1:1) nitric acid for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric volumetric ware and storage

containers should be cleaned by leaching with more dilute acids appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment.

7.3 Sample Digestion

7.3.1 Weigh the Teflon PFA digestion vessel, valve and cap assembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the Teflon PFA sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lb (16 N-m) according to the unit manufacturer's directions. The sample vessel may be connected to an overflow vessel using Teflon PFA connecting tubes. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel. Connect the overflow vessels to the center well of the unit.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

7.3.4 Place the vessels evenly distributed in the turntable of the microwave unit using groups of 2 sample vessels or 6 sample vessels. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, i.e., 3 samples plus 1 blank, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of 2 sample vessels at 344 W for 10 minutes and each group of 6 sample vessels at 574 W for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi).

7.3.4.1 Newer microwave units may be capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest other than two or six samples at a time, the analyst may use different values of power as

long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned polyethylene bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute nitric acid. Filter the sample through quantitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A replicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: The precision of Method 3051, as determined by the statistical examination of interlaboratory test results is as follows:

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206 x$$

in the long run, where x is one result in $\mu\text{g/g}$ (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303 x$$

in the long run, where x is the average of two successive measurements in $\mu\text{g/g}$ (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

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TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN
CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

<u>Element</u>	<u>Repeatability</u>	<u>Reproducibility</u>
Ag	0.195X ^a	0.314X
Al	0.232X	0.444X
B	12.9 ^b	22.6 ^b
Ba	0.238X	0.421X
Be	0.082 ^b	0.082 ^b
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X ^{1/2} ^c	4.02X ^{1/2}
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X ^{1/2}	2.23X ^{1/2}
Zn	3.82X ^{1/2}	7.69X ^{1/2}

^aLog transformed variable based on one-way analysis of variance.

^bRepeatability and reproducibility were independent of concentration .

^cSquare root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

<u>Average Value</u>	<u>Repeatability</u>	<u>Reproducibility</u>
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

all results are in mg/Kg

TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

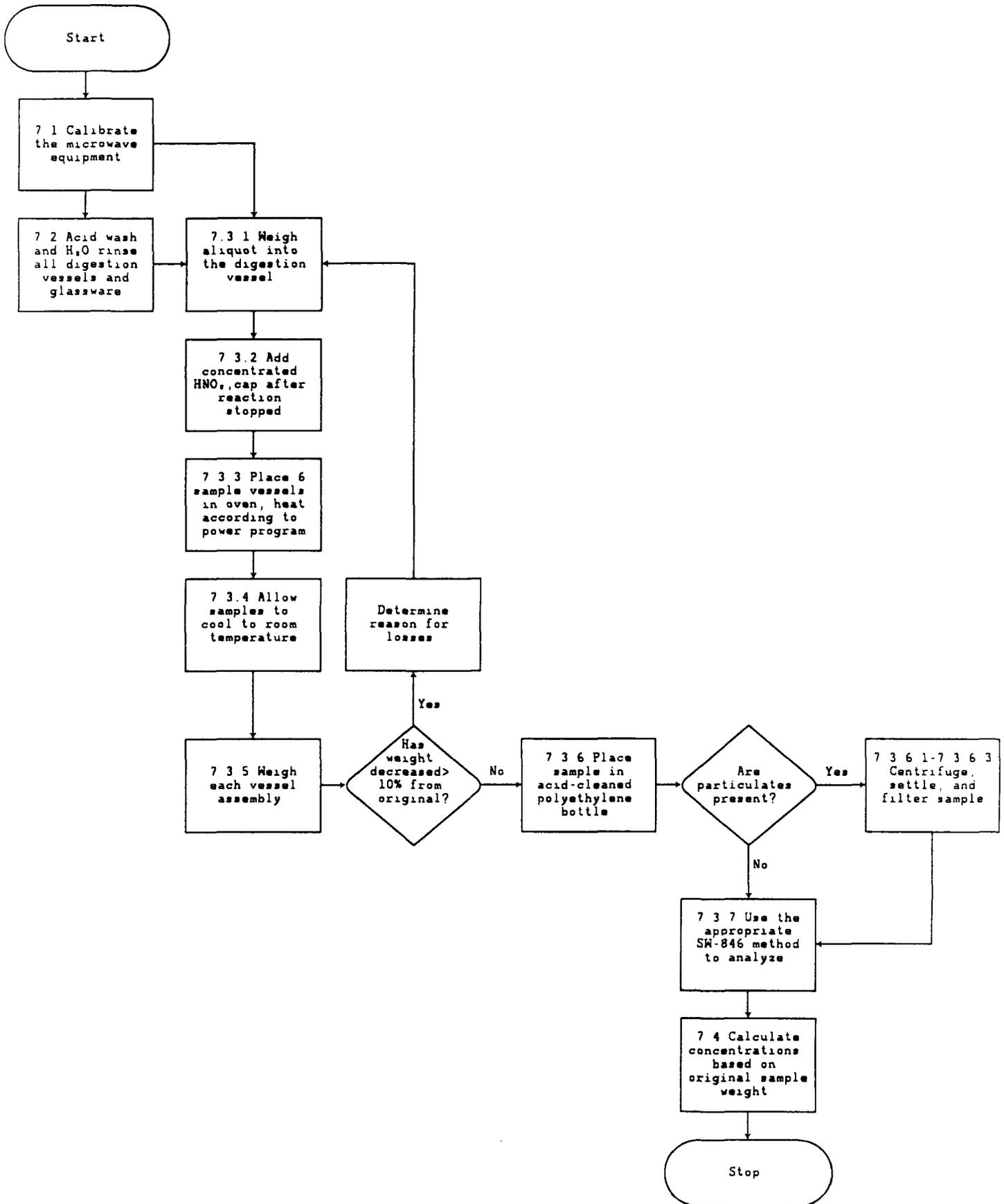
Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias ($\mu\text{g/g}$)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234 \pm 16	--	--	--
Al	296 \pm 4	295 \pm 12	-1	0	No
Cr	298 \pm 5	293 \pm 10	-5	-2	No
Cu	295 \pm 10	289 \pm 9	-6	-2	No
Fe	300 \pm 4	311 \pm 14	+11	+4	No
Mg	297 \pm 3	270 \pm 11	-27	-9	Yes
Mo	292 \pm 11	238 \pm 11	-54	-18	Yes
Ni	303 \pm 7	293 \pm 9	-10	-3	No
Pb	(305)**	279 \pm 8	--	--	--

all values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.

METHOD 3051
MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS
SLUDGES, SOILS, AND OILS



METHOD 3510

SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Step 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step to be used.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

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

4.2 Drying column - 20-mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three-ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two-ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - Glass, 2-mL capacity with Teflon lined screw-cap.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Erlenmeyer flask - 250-mL.

4.9 Syringe - 5-mL.

4.10 Graduated cylinder - 1-liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray.

5.5 Sulfuric acid solution (1:1), H_2SO_4 . Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6 Extraction/exchange solvent - Methylene chloride, hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter (nominal) of sample and transfer it to the separatory funnel. If high concentrations are

anticipated, a smaller volume may be used and then diluted with water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 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 and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520.

7.6 Repeat the extraction two more times using fresh portions of solvent (Steps 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Steps 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.10 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.11 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes.

7.12 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Step 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.13 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Step 7.14 or adjusted to 10.0 mL with the solvent last used.

7.14 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.15 The extract obtained (from either Step 7.13 or 7.14) may now be analyzed for analyte content using a variety of organic techniques. If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw-cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	< 2	none	2-propanol	hexane	1.0	1.0, 10.0 ^a
8060	as received	none	hexane	hexane	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8120	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8250 ^b	> 11	< 2	none	-	-	1.0
8270 ^b	> 11	< 2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

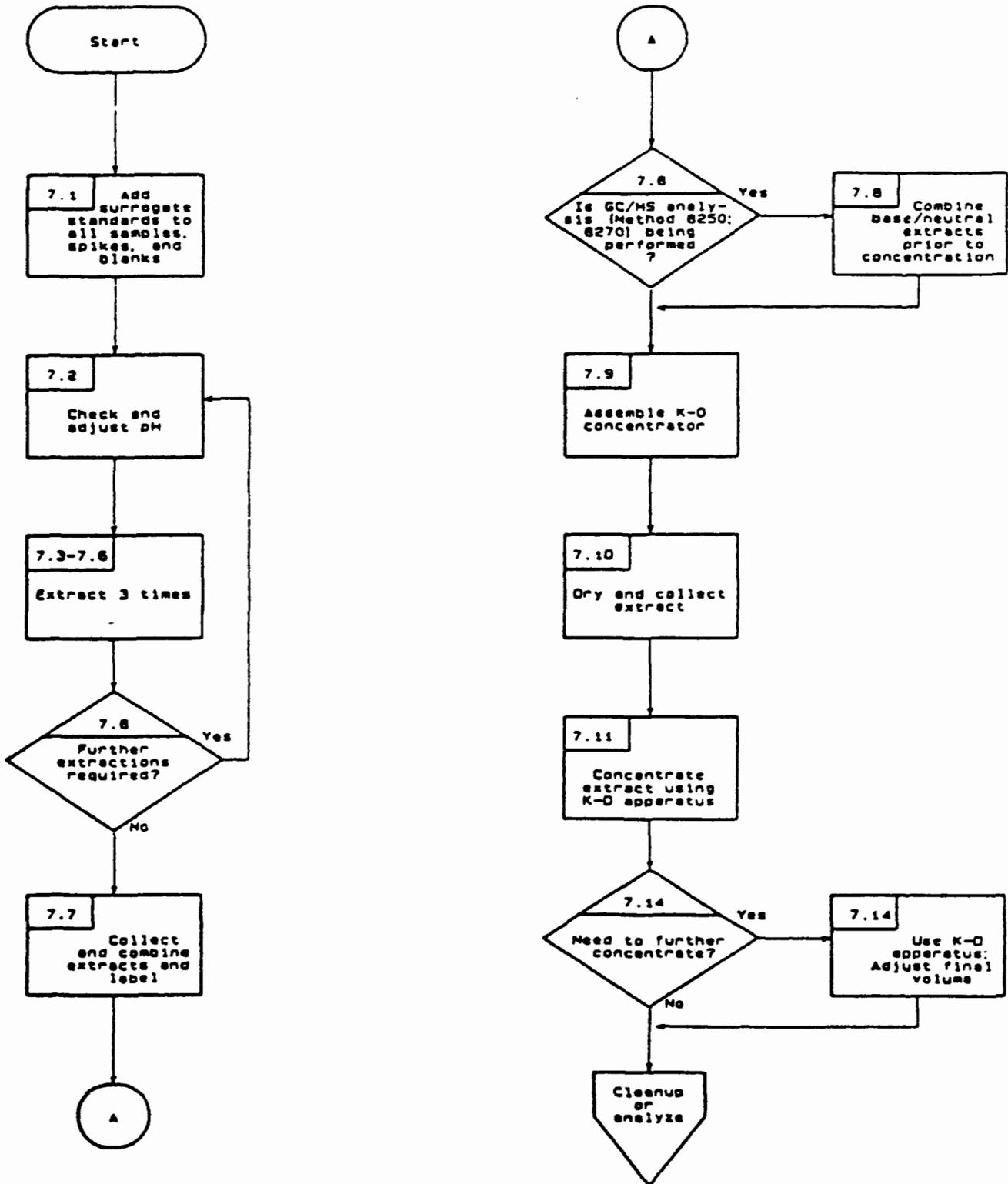
^aPhenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

^bThe specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

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Revision 1
December 1987

METHOD 3510
 SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



METHOD 3520

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Step 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

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

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated, and, as necessary, exchanged into a solvent compatible with the determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor -- Ace Glass Company, Vineland, New Jersey, P/N 6841-10, or equivalent).

4.2 Drying column - 20 mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - 2-mL, glass with Teflon lined screw-cap.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray.

5.5 Sulfuric acid solution (1:1), H_2SO_4 . Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of water.

5.6 Extraction/exchange solvent - Methylene chloride, hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Using a graduated cylinder, measure out 1 liter (nominal) of sample and transfer it to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient water to the extractor to ensure proper operation and extract for 18-24 hours.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated as described in Steps 7.7 through 7.11.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to < 2 with sulfuric acid (1:1). Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8250 or 8270), the acid and base/neutral extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid and base/neutral extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid or base/neutral compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.8 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with

20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.9 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.10 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Step 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.11 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Step 7.12 or adjusted to 10.0 mL with the solvent last used.

7.12 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0 to 2.0 mL, as indicated in Table 1, with solvent.

7.13 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Step 4.3 of this chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw-cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

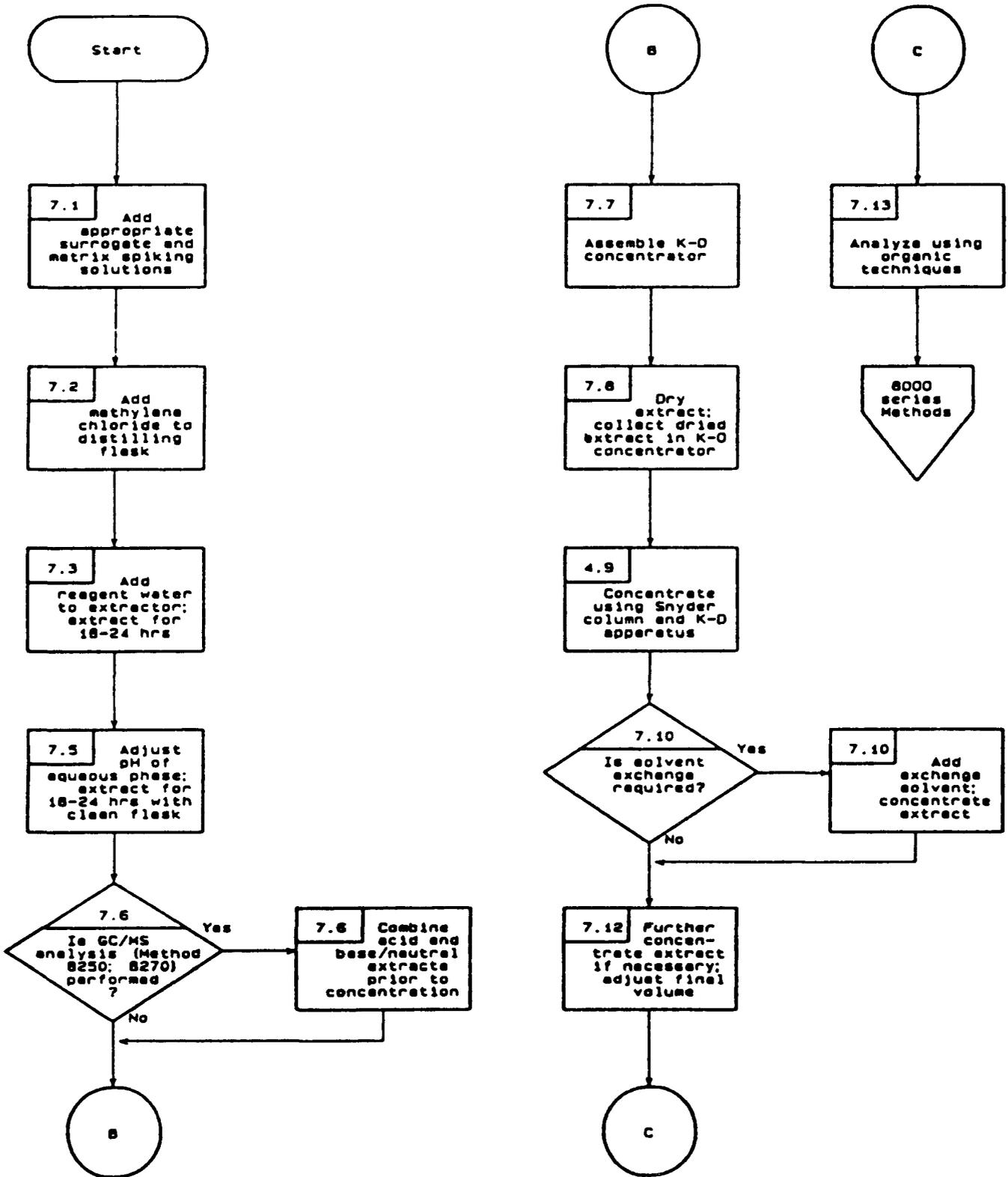
TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	< 2	none	2-propanol	hexane	1.0	1.0, 10.0 ^a
8060	as received	none	hexane	hexane	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8120	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8250 ^b	> 11	< 2	none	-	-	1.0
8270 ^b	> 11	< 2	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0

^aPhenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

^bThe specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3520
CONTINUOUS LIQUID-LIQUID EXTRACTION



METHOD 3540

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated, and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40-mm i.d., with 500-mL round-bottom flask.

4.2 Drying column - 20-mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - Glass, 2-mL capacity, with Teflon lined screw-cap.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5-mL.

4.10 Apparatus for determining percent moisture

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain.

4.11 Apparatus for grinding - If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by washing with methylene chloride followed by heating at 400°C for 4 hours in a shallow tray.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Toluene/Methanol ((10:1) (v/v)), $C_6H_5CH_3/CH_3OH$. Pesticide quality or equivalent.

5.4.1.2 Acetone/Hexane ((1:1) (v/v)), $CH_3COCH_3/CH_3(CH_2)_4CH_3$. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2 . Pesticide quality or equivalent.

5.5 Exchange solvents - Hexane, 2-propanol, cyclohexane, acetonitrile (pesticide quality or equivalent).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1-mm sieve or can be extruded through a 1-mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.2 Determination of percent moisture - In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ moisture} = \frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/uL of each base/neutral analyte and 200 ng/uL of each acid analyte in the extract to be analyzed (assuming a 1 uL injection). If Method 3640, Gel-permeation cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place 300 mL of the extraction solvent (Step 5.3) into a 500-mL round-bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Step 7.6, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Step 7.9 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.12 The extracts obtained may now be analyzed for analyte content using a variety of organic techniques (see Step 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with Teflon lined screw-cap and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

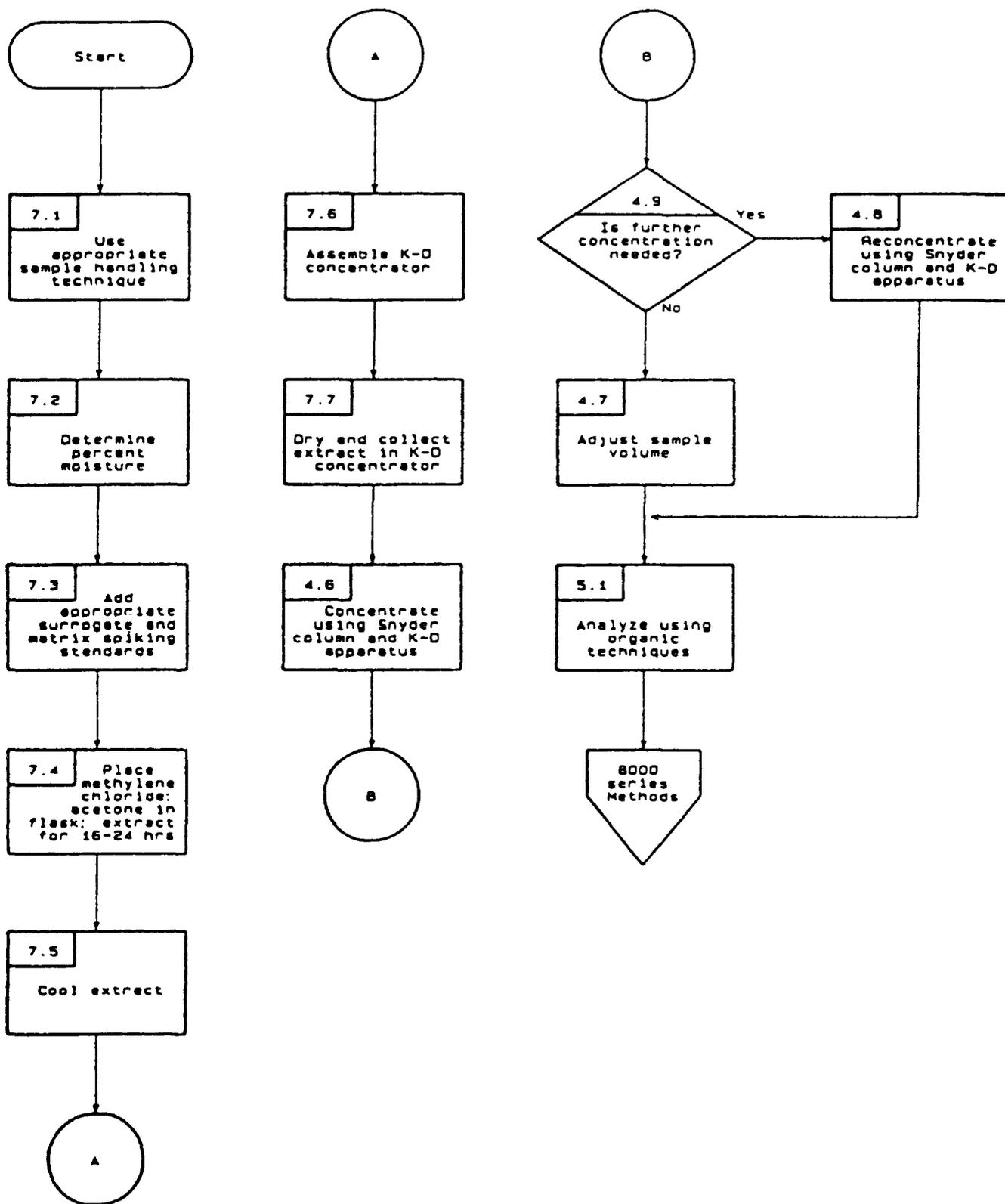
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 ^a	as received	2-propanol	hexane	1.0	1.0, 10.0 ^b
8060	as received	hexane	hexane	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8120	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8250 ^{a, c}	as received	none	-	-	1.0
8270 ^{a, c}	as received	none	-	-	1.0
8310	as received	acetonitrile	-	-	1.0

^a To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

^b Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3540
SOXHLET EXTRACTION



METHOD 3600

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 General

1.1.1 Injection of extracts into a gas or liquid chromatograph can cause extraneous peaks, deterioration of peak resolution and column efficiency, and loss of detector sensitivity and can greatly shorten the lifetime of expensive columns. The following techniques have been applied to extract purification: partitioning between immiscible solvents; adsorption chromatography; gel permeation chromatography; chemical destruction of interfering substances with acid, alkali, or oxidizing agents; and distillation. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.1.2 It is an unusual situation (e.g. with some water samples) when extracts can be directly determined without further treatment. Soil and waste extracts often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.2 Specific

1.2.1 Adsorption column chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity.

1.2.2 Acid-base partitioning - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols.

1.2.3 Gel permeation chromatography (GPC) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Hazardous Substance Lists. GPC is usually not applicable for eliminating extraneous peaks on a chromatogram which interfere with the analytes of interest.

1.2.4 Sulfur cleanup - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.2.5 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should follow a similar elution pattern.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Step 2.3.3, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 In most cases, the extracted sample is then analyzed by one of the determinative methods available in Step 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes (e.g. Method 8060, gas chromatography of phthalate esters, recommends using either Method 3610

(Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis). However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure (Step 4.3 of this Chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples.

8.2 For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative ^a Method	Cleanup Method Option
Phenols	8040	3630 ^b , 3640, 3650, 8040 ^c
Phthalate esters	8060	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080	3620, 3640, 3660
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100	3611, 3630, 3640
Chlorinated hydrocarbons	8120	3620, 3640
Organophosphorous pesticides	8140	3620
Chlorinated herbicides	8150	8150 ^d
Priority pollutant semivolatiles	8250, 8270	3640, 3650, 3660
Petroleum waste	8250, 8270	3611, 3650

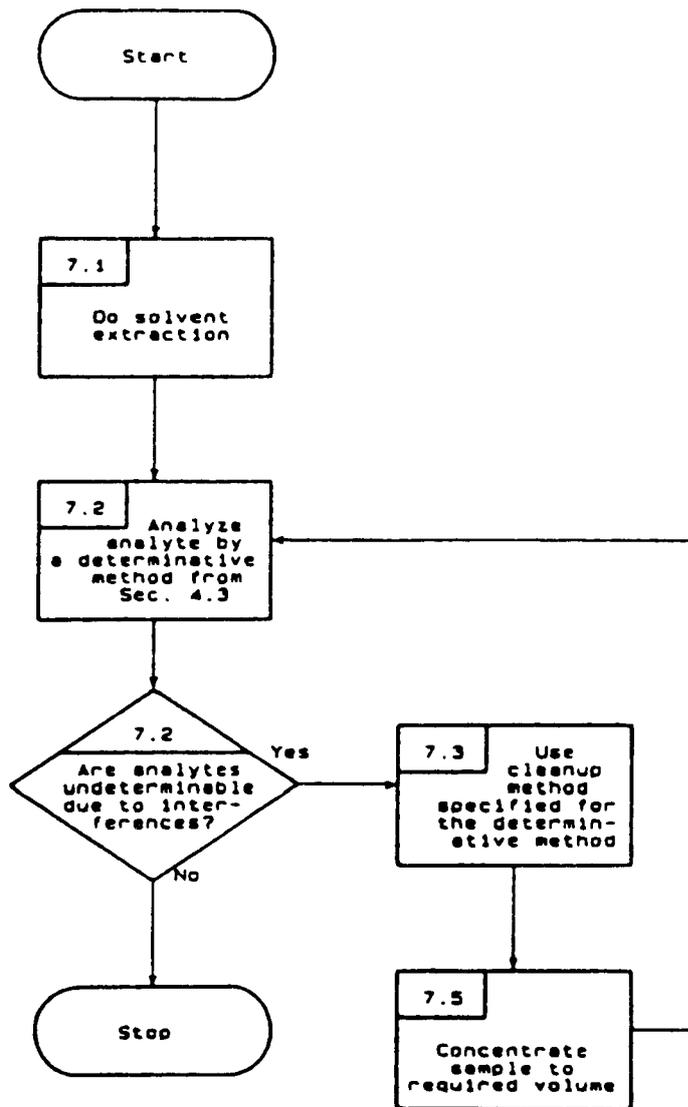
^a The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

^b Cleanup applicable to derivatized phenols.

^c Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

^d Method 8150 incorporates an acid-base cleanup step as an integral part of the method.

METHOD 3600
CLEANUP



METHOD 3650

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formerly Method 3530 in the second edition of this manual.

1.2 This is a liquid-liquid partitioning cleanup method to separate acid analytes, e.g. organic acids and phenols, from base/neutral analytes, e.g. amines, aromatic hydrocarbons, and halogenated organic compounds, using pH adjustment. It may be used for cleanup of petroleum waste prior to alumina cleanup. Specific examples of compounds that are separated by this method are in Table 1.

2.0 SUMMARY OF METHOD

2.1 The solvent extract from a prior solvent extraction method is shaken with water that is strongly basic. The acid analytes partition into the aqueous layer, whereas, the basic and neutral compounds stay in the organic solvent. The base/neutral fraction is concentrated and is then ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and is then ready for analysis of the acid analytes.

3.0 INTERFERENCES

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

3.2 A method blank must be run for the compounds of interest prior to use of the method. The interferences must be below the method detection limit before this method is applied to actual samples.

4.0 APPARATUS AND MATERIALS

4.1 Drying column - 20 mm i.d. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to clean after highly contaminated extracts have been passed through them. Columns without frits are recommended. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent (Table 1) prior to packing the column with adsorbent.

4.2 Kuderna-Danish (K-D) apparatus (Kontes K-570025-0500)

4.2.1 Concentrator tube - 10-mL graduated (Kontes K570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of the extracts.

4.2.2 Evaporation flask - 500-mL (K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Vials - Glass, 2-mL capacity with Teflon lined screw-cap.

4.4 Water bath - Heated, concentric ring cover, temperature control of $\pm 2^{\circ}\text{C}$. Use this bath in a hood.

4.5 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 pH indicator paper - pH range including the desired extraction pH.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Methylene chloride, CH_2Cl_2 . Pesticide quality or equivalent.

5.4 Sodium hydroxide (10N), NaOH. Dissolve 40 g of sodium hydroxide in 100 mL of water.

5.5 Sulfuric acid (1:1 v/v in water), H_2SO_4 . Slowly add 50 mL H_2SO_4 to 50 mL of water.

5.6 Sodium sulfate, Na_2SO_4 . Granular, anhydrous, purify by rinsing with acetone followed by the elution solvent and then drying at 200°C for 4 hours.

5.7 Acetone, CH_3COCH_3 . Pesticide quality or equivalent.

5.8 Methanol, CH_3OH . Pesticide quality or equivalent.

5.9 Ethyl ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$. Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Place 10 mL of the solvent extract from a prior extraction procedure into a 125-mL separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Slowly add 20 mL of prechilled water which has been previously adjusted to a pH of 12-13 with 10N sodium hydroxide.

7.4 Seal and shake the separatory funnel for at least 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once.

7.5 Allow the organic layer to separate from the aqueous phase for a minimum of 10 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, and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

7.6 Separate the aqueous phase and transfer it to a 125-mL Erlenmeyer flask. Repeat the extraction two more times using fresh 20 mL aliquots of dilute sodium hydroxide (pH 12-13). Combine the aqueous extracts.

7.7 Water soluble organic acids and phenols will be primarily in the aqueous phase. Base/neutral analytes will be in the methylene chloride. If the analytes are only in the aqueous phase, discard the methylene chloride and proceed to Step 7.8. If the analytes are only in the methylene chloride, discard the aqueous phase and proceed to Step 7.10.

7.8 Externally cool the 125-mL Erlenmeyer flask with ice while adjusting the aqueous phase to a pH of 1-2 with sulfuric acid (1:1). Transfer the cool aqueous phase to a clean 125-mL separatory funnel. Add 20 mL of methylene chloride to the separatory funnel and shake for at least 2 minutes. Allow the methylene chloride to separate from the aqueous phase and collect the methylene chloride in an Erlenmeyer flask.

7.9 Add 20-mL of methylene chloride to the separatory funnel and extract at pH 1-2 a second time. Perform a third extraction in the same manner combining the extracts in the Erlenmeyer flask.

7.10 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporation flask.

7.11 Dry both acid and base/neutral fractions by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried fractions in K-D concentrators. Rinse the Erlenmeyer flasks which contained the solvents and the columns with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 Concentrate both acid and base/neutral fractions as follows: Add one or two boiling chips to the flask and attach a three ball macro-Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (80-90°C) so that the concentrator tube is partially immersed in the warm water. 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 volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride.

7.13 Add another one or two boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top of the column. Place the K-D apparatus in a hot water bath (80-90°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 the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to cool. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride. Adjust the final volume to 1 mL with methylene chloride.

7.14 The acid fraction is now ready for analysis. If the base/neutral fraction requires further cleanup by the alumina column cleanup for petroleum waste (Method 3611), the solvent may have to be changed to hexane. To the 1 mL base/neutral fraction, 5 mL of hexane should be added, and this mixture concentrated to 1 mL using the micro K-D apparatus (repeat 2 more times). If no further cleanup of the base/neutral extract is required, it is also ready for analysis.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and Method 3600 for cleanup procedures.

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

8.3 For samples that are cleaned using this method, the associated quality control samples must be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

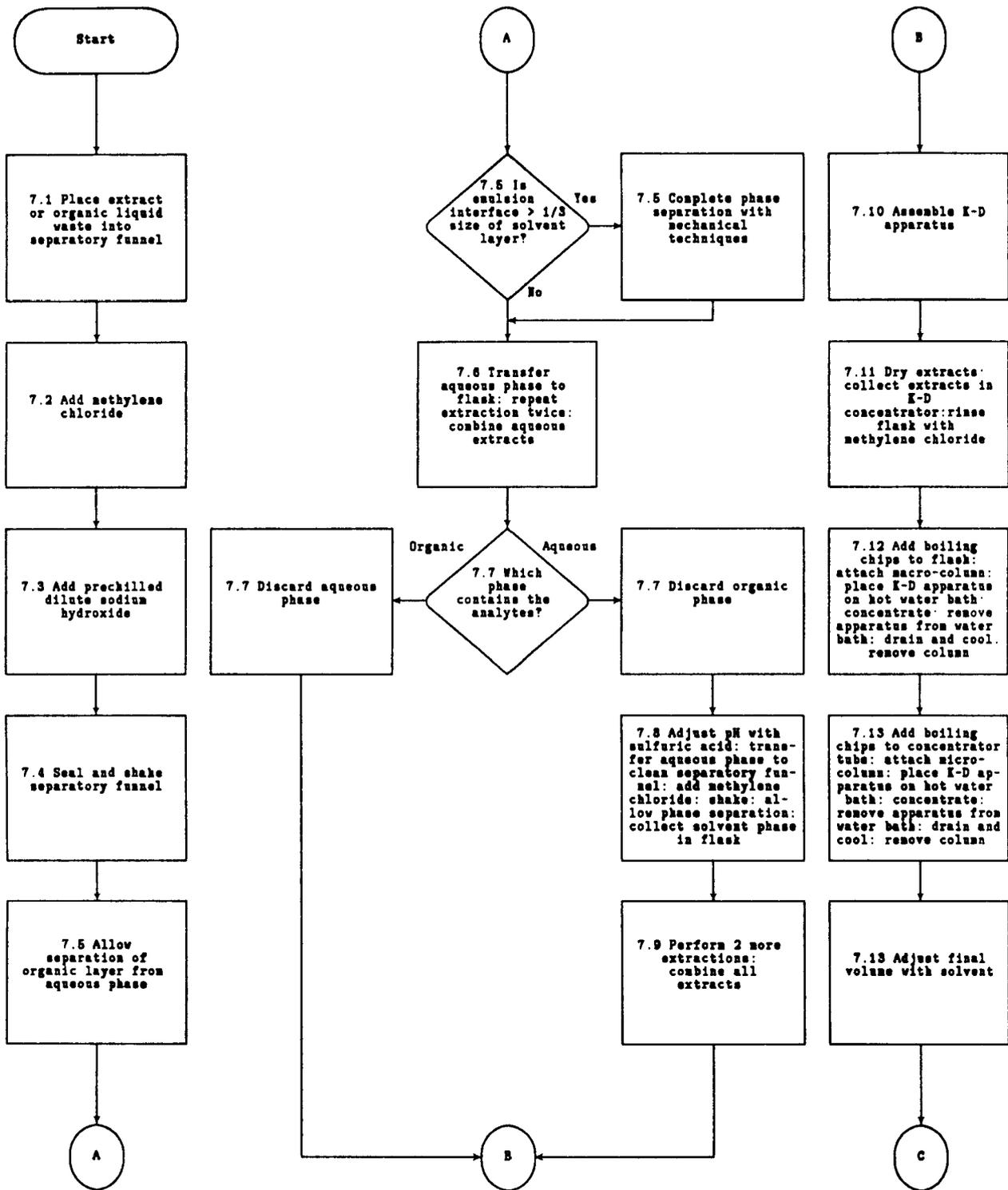
10.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. Environmental Protection Agency. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1987; SW-846; 955-001-00000-1.
2. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1982; EPA-600/4-82-057.
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

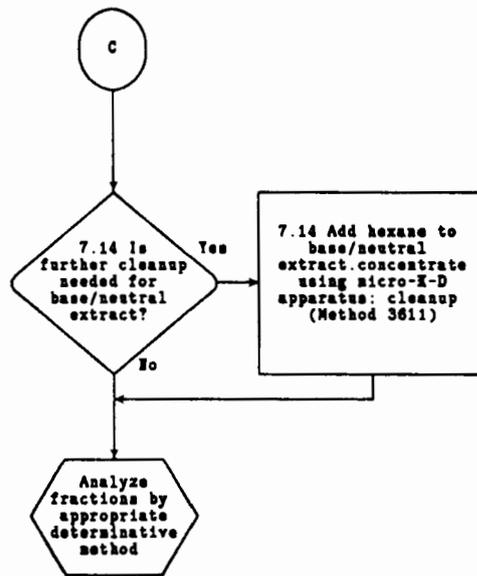
TABLE 1.
ANALYTES WHICH CAN BE PARTITIONED BY METHOD 3650

Compound	Chemical Abstracts Service Registry Number	Fraction
Benz(a)anthracene	56-55-3	Base-neutral
Benzo(a)pyrene	50-32-8	Base-neutral
Benzo(b)fluoranthene	205-99-2	Base-neutral
Chlordane	57-74-9	Base-neutral
Chlorinated dibenzodioxins		Base-neutral
2-Chlorophenol	95-57-8	Acid
Chrysene	218-01-9	Base-neutral
Creosote	8001-58-9	Base-neutral and Acid
Cresol(s)		Acid
Cresylic acid(s)		Acid
Dichlorobenzene(s)		Base-neutral
Dichlorophenoxyacetic acid	94-75-7	Acid
2,4-Dimethylphenol	105-67-9	Acid
Dinitrobenzene	25154-54-5	Base-neutral
4,6-Dinitro- <i>o</i> -cresol	534-52-1	Acid
2,4-Dinitrotoluene	121-14-2	Base-neutral
Heptachlor	76-44-8	Base-neutral
Hexachlorobenzene	118-74-1	Base-neutral
Hexachlorobutadiene	87-68-3	Base-neutral
Hexachloroethane	67-72-1	Base-neutral
Hexachlorocyclopentadiene	77-47-4	Base-neutral
Naphthalene	91-20-3	Base-neutral
Nitrobenzene	98-95-3	Base-neutral
4-Nitrophenol	100-02-7	Acid
Pentachlorophenol	87-86-5	Acid
Phenol	108-95-2	Acid
Phorate	298-02-2	Base-neutral
2-Picoline	109-06-8	Base-neutral
Pyridine	110-86-1	Base-neutral
Tetrachlorobenzene(s)		Base-neutral
Tetrachlorophenol(s)		Acid
Toxaphene	8001-35-2	Base-neutral
Trichlorophenol(s)		Acid
2,4,5-TP (Silvex)	93-72-1	Acid

**METHOD 3650
ACID-BASE PARTITION CLEANUP**



METHOD 3650
(Continued)



METHOD 5030

PURGE-AND-TRAP

1.0 SCOPE AND APPLICATION

1.1 This method describes sample preparation and extraction for the analysis of volatile organics by a purge-and-trap procedure. The gas chromatographic determinative steps are found in Methods 8010, 8015, 8021, and 8030. Although applicable to Method 8240, the purge-and-trap procedure is already incorporated into Method 8240.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system.

1.4 This method also describes the preparation of water-miscible liquids, solids, wastes, and soil/sediments for analysis by the purge-and-trap procedure.

2.0 SUMMARY OF METHOD

2.1 The purge-and-trap process - An inert gas is bubbled through the solution at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a specially designed purging chamber. It is then analyzed by purge-and-trap GC following the normal water method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from

contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, 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 and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A field reagent blank prepared from reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination; therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-uL, 25-uL, 100-uL, 250-uL, 500-uL, and 1,000 uL: These syringes should be equipped with a 20-gauge (0.006-in i.d.) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Syringe - 5-mL, gas-tight with shutoff valve.

4.4 Balance - Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.5 Glass scintillation vials - 20-mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.6 Volumetric flasks - 10-mL and 100-mL, class A with ground-glass stoppers.

4.7 Vials - 2-mL, for GC autosampler.

4.8 Spatula - Stainless steel.

4.9 Disposable pipets - Pasteur.

4.10 Purge-and-trap device - The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.10.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

4.10.2 The trap must be at least 25 cm long and have an inside diameter of at least 0.105 in. Starting from the inlet, the trap must contain the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.10.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.10.5 Trap Packing Materials

4.10.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

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

4.10.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, by crushing through 26 mesh screen.

4.11 Heater or heated oil bath - Capable of maintaining the purging chamber to within 1°C over a temperature range from ambient to 100°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Methanol, CH₃OH. Pesticide quality or equivalent. Store away from other solvents.

5.4 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

5.4.1 Tetraglyme (tetraethylene glycol dimethylether, Aldrich #17, 240-5 or equivalent), C₈H₁₈O₅. Purify by treatment at reduced pressure in a rotary evaporator. The tetraglyme should have a peroxide content of less than 5 ppm as indicated by EM Quant Test Strips (available from Scientific Products Co., Catalog No. P1126-8 or equivalent).

CAUTION: Glycol ethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

Peroxides may be removed by passing the tetraglyme through a column of activated alumina. The tetraglyme is placed in a round bottom flask equipped with a standard taper joint, and the flask is affixed to a rotary evaporator. The flask is immersed in a water bath at 90-100°C and vacuum is maintained at < 10 mm Hg for at least two hours using a two-stage mechanical pump. The vacuum system is equipped with an all-glass trap, which is maintained in a dry ice/methanol bath. Cool the tetraglyme to ambient temperature and add 0.1 mg/mL of 2,6-di-tert-butyl-4-methyl-phenol to prevent peroxide formation. Store the tetraglyme in a tightly sealed screw-cap bottle in an area that is not contaminated by solvent vapors.

5.4.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, a water/tetraglyme blank must be analyzed.

5.5 Polyethylene glycol, H(OCH₂CH₂)_nOH. Free of interferences at the detection limit of the analytes.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this Chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Initial calibration - Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, Step 7.4, while the specific determinative methods and Method 3500 give details on preparation of standards.

7.1.1 Assemble a purge-and-trap device that meets the specification in Step 4.10. Condition the trap overnight at 180°C in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 minutes while backflushing at 180°C with the column at 220°C.

7.1.2 Connect the purge-and-trap device to a gas chromatograph.

7.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. (Use freshly prepared stock solutions when preparing the calibration standards for the initial calibration.) Add 5.0 mL of water to the purging device. The water is added to the purging device using a 5-mL glass syringe fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10- μ L or 25- μ L microsyringe equipped with a long needle (Step 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 μ L of the internal standard solution. Close the 2-way syringe valve at the sample inlet.

7.1.4 Carry out the purge-and-trap analysis procedure using the specific conditions given in Table 1.

7.1.5 Calculate response factors or calibration factors for each analyte of interest using the procedure described in Method 8000, Step 7.4.

7.1.6 The average RF must be calculated for each compound. A system performance check should be made before this calibration curve is used. If the purge-and-trap procedure is used with Method 8010, the following five compounds are checked for a minimum average response factor: chloromethane; 1,1-dichloroethane; bromoform; 1,1,2,2-tetrachloroethane; and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs

of 0.4-0.6 and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

1. Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

2. Bromoform - This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

3. Tetrachloroethane and 1,1-dichloroethane - These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2 On-going calibration - Refer to Method 8000, Steps 7.4.2.3 and 7.4.3.4 for details on continuing calibration.

7.3 Sample preparation

7.3.1 Water samples

7.3.1.1 Screening of the sample prior to purge-and-trap analysis will provide guidance on whether sample dilution is necessary and will prevent contamination of the purge-and-trap system. Two screening techniques that can be utilized are: the use of an automated headspace sampler (modified Method 3810), interfaced to a gas chromatograph (GC), equipped with a photo ionization detector (PID), in series with an electrolytic conductivity detector (ECD); and extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC with a FID and/or an ECD.

7.3.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.3.1.3 Assemble the purge-and-trap device. The operating conditions for the GC are given in Section 7.0 of the specific determinative method to be employed.

7.3.1.4 Daily GC calibration criteria must be met (Method 8000, Step 7.4) before analyzing samples.

7.3.1.5 Adjust the purge gas flow rate (nitrogen or helium) to that shown in Table 1, on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.3.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the

sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.3.1.7 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.3.1.7.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.3.1.7.2 Calculate the approximate volume of water to be added to the volumetric flask selected and add slightly less than this quantity of water to the flask.

7.3.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Step 7.3.1.5 into the flask. Aliquots of less than 1-mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.3.1.7.4 Fill a 5-mL syringe with the diluted sample as in Step 7.3.1.5.

7.3.1.8 Add 10.0 uL of surrogate spiking solution (found in each determinative method, Section 5.0) and, if applicable, 10 uL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.1.9 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.

7.3.1.10 Close both valves and purge the sample for the time and at the temperature specified in Table 1.

7.3.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin

the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C while backflushing the trap with inert gas between 20 and 60 mL/min for the time specified in Table 1.

7.3.1.12 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5-mL flushes of water (or methanol followed by water) to avoid carryover of pollutant compounds into subsequent analyses.

7.3.1.13 After desorbing the sample, 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. The trap temperature should be maintained at 180°C for Methods 8010 and 8020, and 210°C for Methods 8015 and 8030. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 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.

7.3.1.14 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by a blank water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences.

7.3.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.3.2 Water-miscible liquids

7.3.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with water.

7.3.2.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample to a 100-mL volumetric flask and diluting to volume with water. Transfer immediately to a 5-mL gas-tight syringe.

7.3.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with water by adding at least 20 μ L, but not more than 100- μ L of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC analysis. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. See Step 7.3.1.1 for recommended screening techniques. Use the screening data to determine whether to use the low-level method (0.005-1 mg/kg) or the high-level method (> 1 mg/kg).

7.3.3.1 Low-level method - This is designed for samples containing individual purgeable compounds of < 1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a heated sediment/soil sample mixed with water containing the surrogate and, if applicable, internal and matrix spiking standards. Analyze all reagent blanks and standards under the same conditions as the samples.

7.3.3.1.1 Use a 5-g sample if the expected concentration is < 0.1 mg/kg or a 1-g sample for expected concentrations between 0.1 and 1 mg/kg.

7.3.3.1.2 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve must be prepared and used for the quantitation of all samples analyzed with the low-level method. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature for Methods 8010 and 8020.

7.3.3.1.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 uL each of surrogate spiking solution and internal standard solution to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) Matrix spiking solutions, if indicated, should be added (10 uL) to the sample at this time.

7.3.3.1.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Step 7.3.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.3.3.1.5 In certain cases, sample results are desired based on a dry-weight basis. When such data is desired, a portion of sample for moisture determination should be weighed out at the same time as the portion used for analytical determination. Immediately after weighing the sample for

extraction, weigh 5-10 g of the sample into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ moisture} = \frac{\text{g of sample} - \text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3.3.1.6 Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

NOTE: Prior to the attachment of the purge device, Steps 7.3.3.1.4 and 7.3.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

7.3.3.1.7 Heat the sample to 40°C ± 1°C (Methods 8010 and 8020) or to 85°C ± 2°C (Methods 8015 and 8030) and purge the sample for the time shown in Table 1.

7.3.3.1.8 Proceed with the analysis as outlined in Steps 7.3.1.11-7.3.1.15. Use 5 mL of the same water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the high-level method must be followed.

7.3.3.2 High-level method - The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes (i.e. petroleum and coke wastes) that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to water containing surrogate and, if applicable, internal and matrix spiking standards. This is purged at the temperatures indicated in Table 1. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.3.3.2.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20-mL vial. Use a top-loading balance. Note and record the actual weight to 0.1 gram and determine the percent moisture of the sample using the procedure in Step 7.3.3.1.5. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Pipet 10.0 mL of solvent into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.3.3.2.2 Quickly add 9.0 mL of appropriate solvent; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 minutes.

NOTE: Steps 7.3.3.2.1 and 7.3.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed of. Transfer approximately 1 mL of appropriate solvent to a separate GC vial for use as the method blank for each set of samples. These extracts may be stored at 4°C in the dark, prior to analysis.

7.3.3.2.4 The GC system should be set up as in Section 7.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to water.

7.3.3.2.5 Table 2 can be used to determine the volume of solvent extract to add to the 5 mL of water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a high-level sample, start with 100 μ L. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3.2.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 μ L of internal standard solution. Also add the volume of solvent extract determined in Step 7.3.3.2.5 and a volume of extraction or dissolution solvent to total 100 μ L (excluding solvent in standards).

7.3.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/solvent sample into the purging chamber.

7.3.3.2.8 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 μ L of solvent to simulate the sample conditions.

7.3.3.2.9 For a matrix spike in the high-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution and 1.0 mL of matrix spike solution.

Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Step 7.3.3.2.6).

7.4 Sample analysis

7.4.1 The samples prepared by this method may be analyzed by Methods 8010, 8015, 8020, 8021, and 8030. Refer to these methods for appropriate analysis conditions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 for sample preparation procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a calibration 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 reagent blank should be processed as a safe-guard against chronic laboratory contamination. The blanks should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Spiked samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the spiked samples do not indicate sufficient sensitivity to detect < 1 ug/g of the analytes in the sample, then the sensitivity of the instrument should be increased, or the sample should be subjected to additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. Gebhart, J.E.; Lucas, S.V.; Naber, S.J.; Berry, A.M.; Danison, T.H.; Burkholder, H.M. "Validation of SW-846 Methods 8010, 8015, and 8020"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, July 1987, Contract No. 68-03-1760.
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method				
	8010	8015	8020	8021	8030
Purge gas	Nitrogen or Helium				
Purge gas flow rate (mL/min)	40	20	40	25-40	20
Purge time (min)	11.0 ± 0.1	15.0 ± 0.1	12.0 ± 0.1	11.0 ± 0.1	15.0 ± 0.1
Purge temperature (°C)	Ambient	85 ± 2	Ambient	Ambient	85 ± 2
Desorb temperature (°C)	180	180	180	180	180
Backflush inert gas flow (mL/min)	20-60	20-60	20-60	6	20-60
Desorb time (min)	4	1.5	4	4 ± 0.1	1.5

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TABLE 2.
 QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS
 OF HIGH-LEVEL SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract ^a
500-10,000 ug/kg	100 uL
1,000-20,000 ug/kg	50 uL
5,000-100,000 ug/kg	10 uL
25,000-500,000 ug/kg	100 uL of 1/50 dilution ^b

Calculate appropriate dilution factor for concentrations exceeding this table.

^aThe volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a volume of 100 uL added to the syringe.

^bDilute an aliquot of the methanol extract and then take 100 uL for analysis.

FIGURE 1.
PURGING CHAMBER

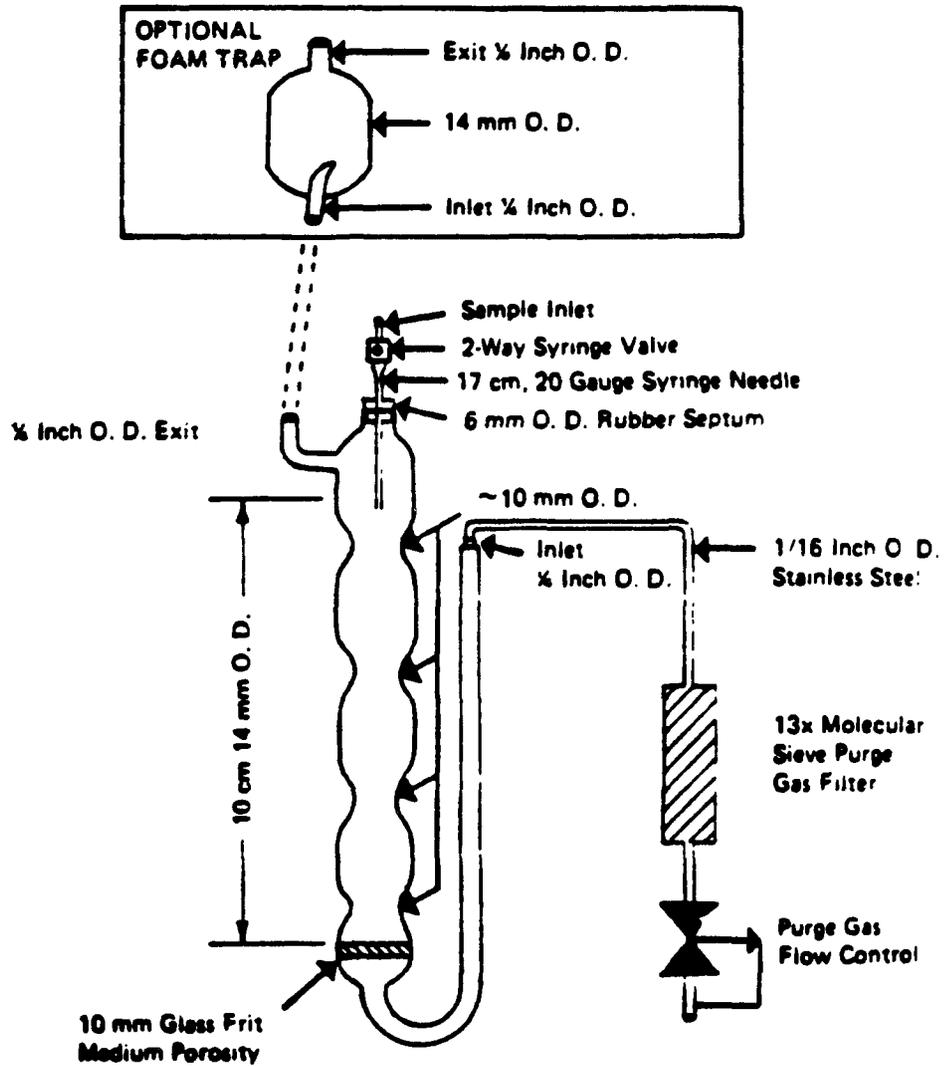


FIGURE 2.
TRAP PACKING MATERIALS AND CONSTRUCTION FOR METHOD 8010

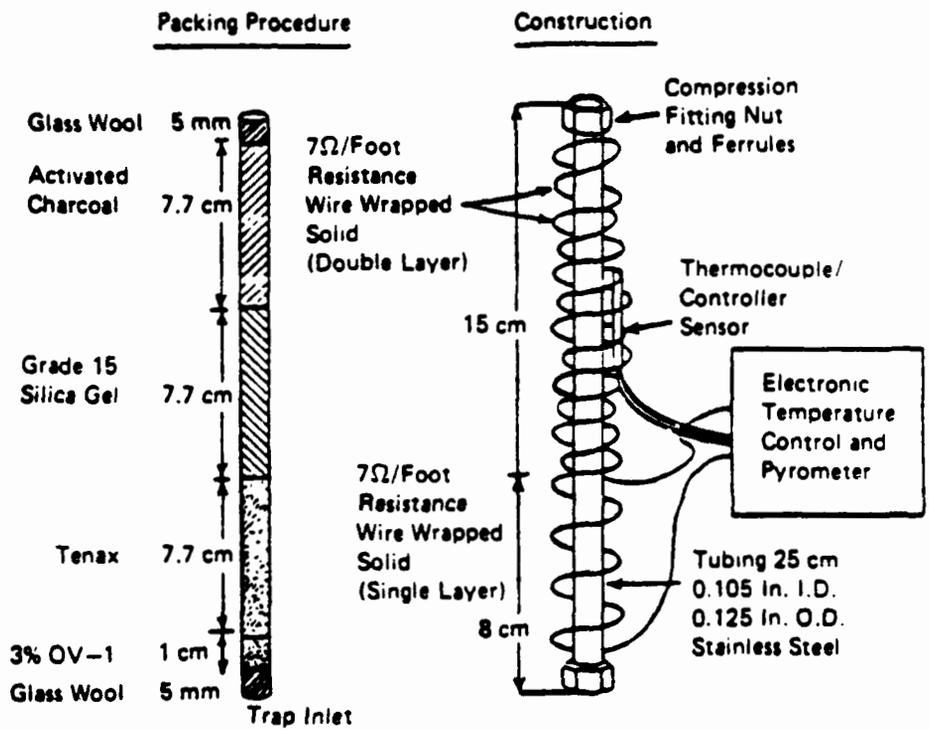


FIGURE 3.
TRAP PACKING MATERIALS AND CONSTRUCTION FOR METHODS 8020 AND 8030

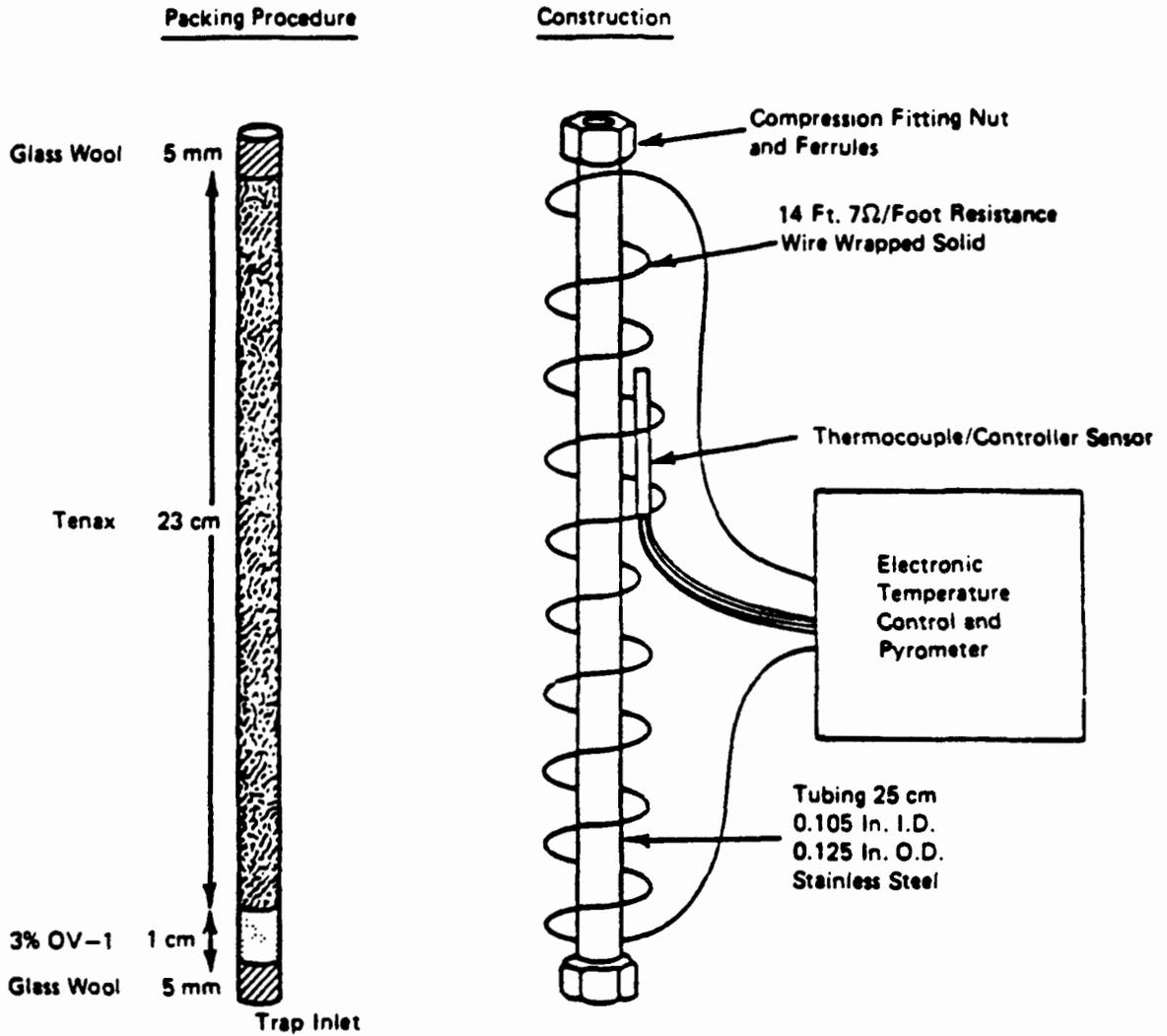


FIGURE 4.
 PURGE-AND-TRAP SYSTEM, PURGE-SORB MODE,
 FOR METHODS 8010, 8020, AND 8030

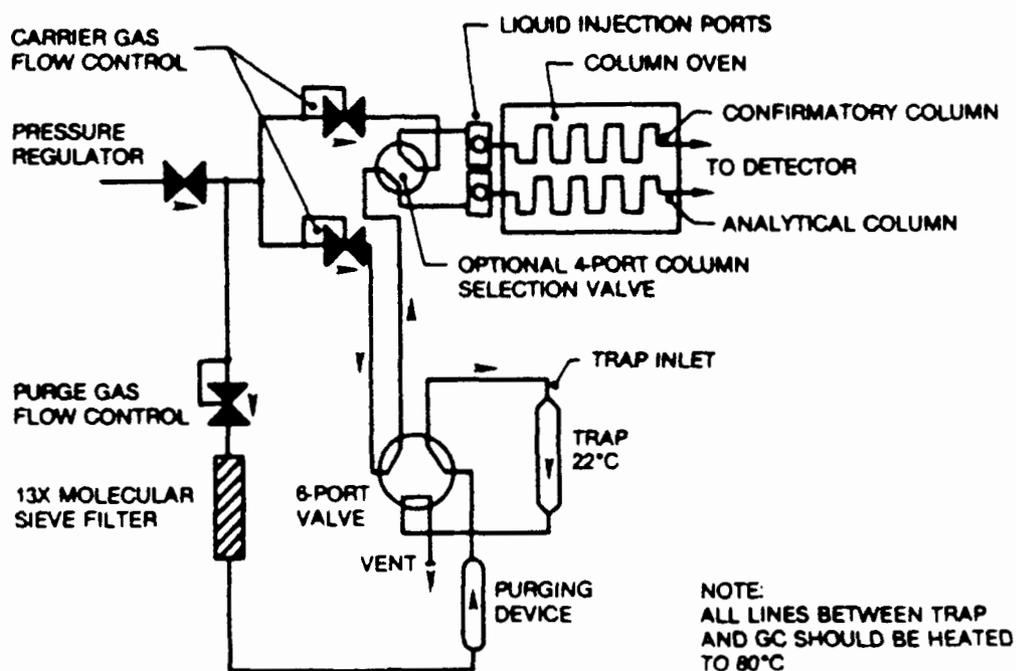
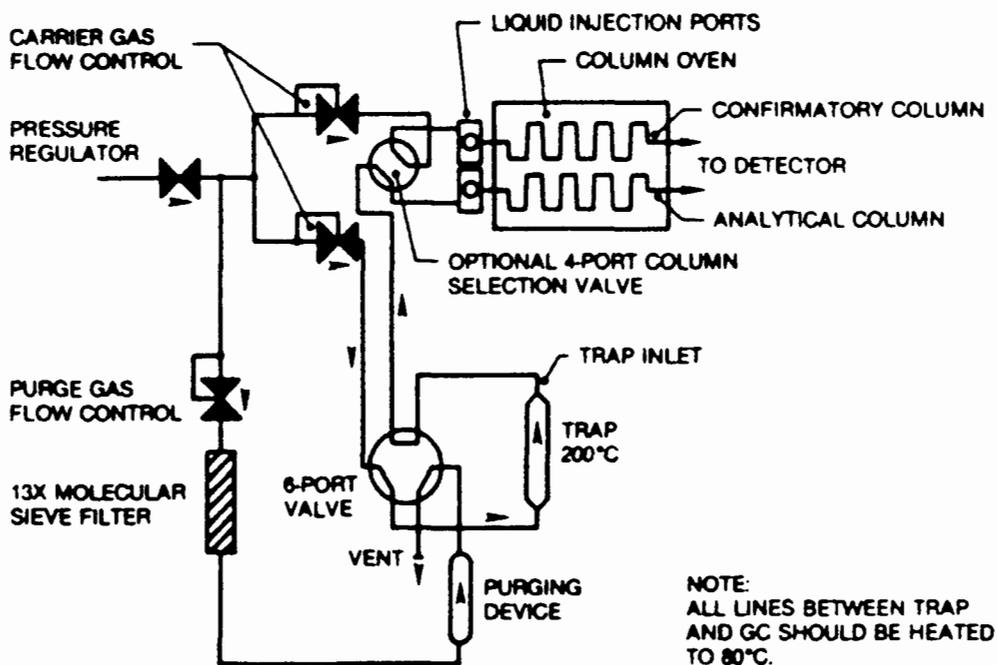
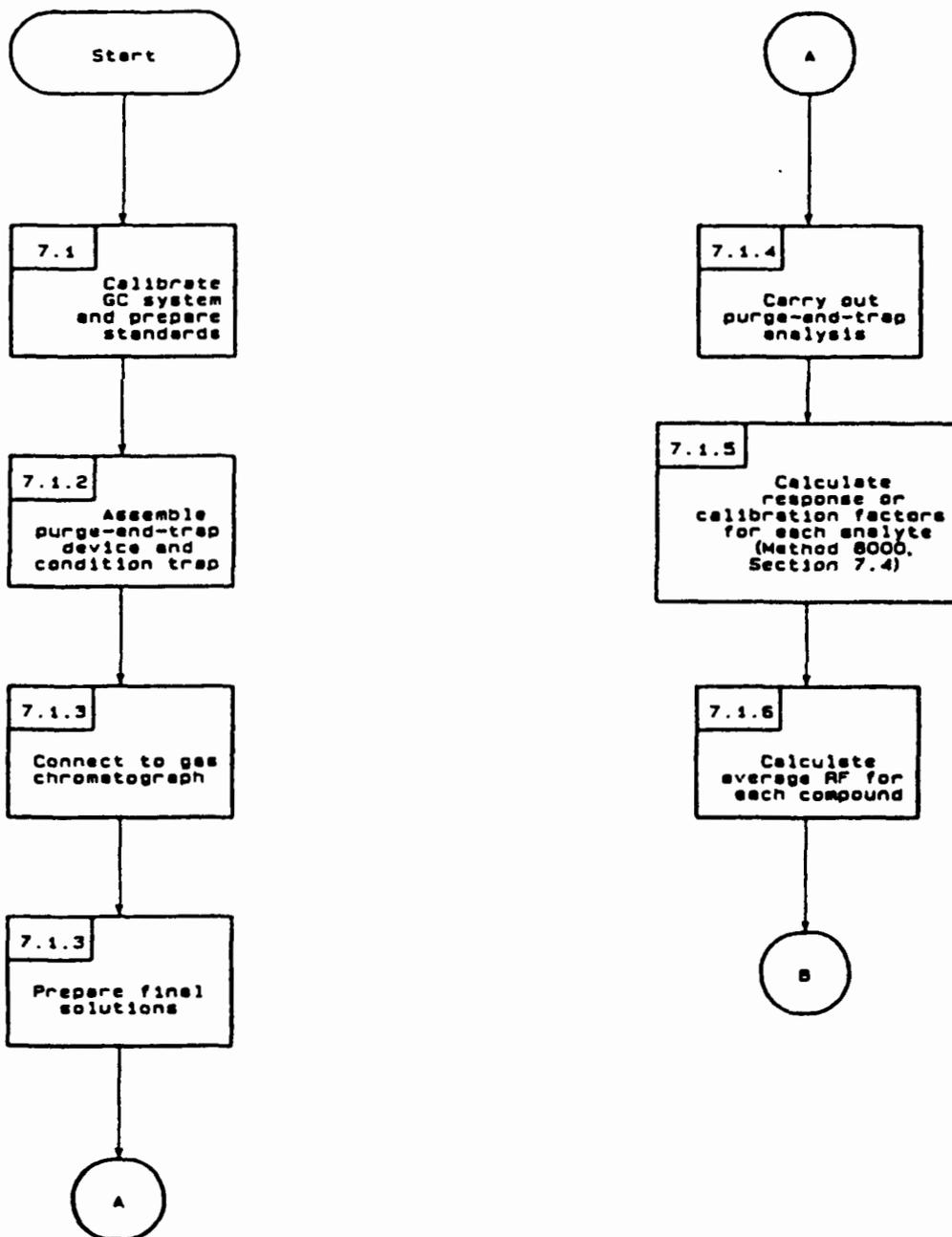


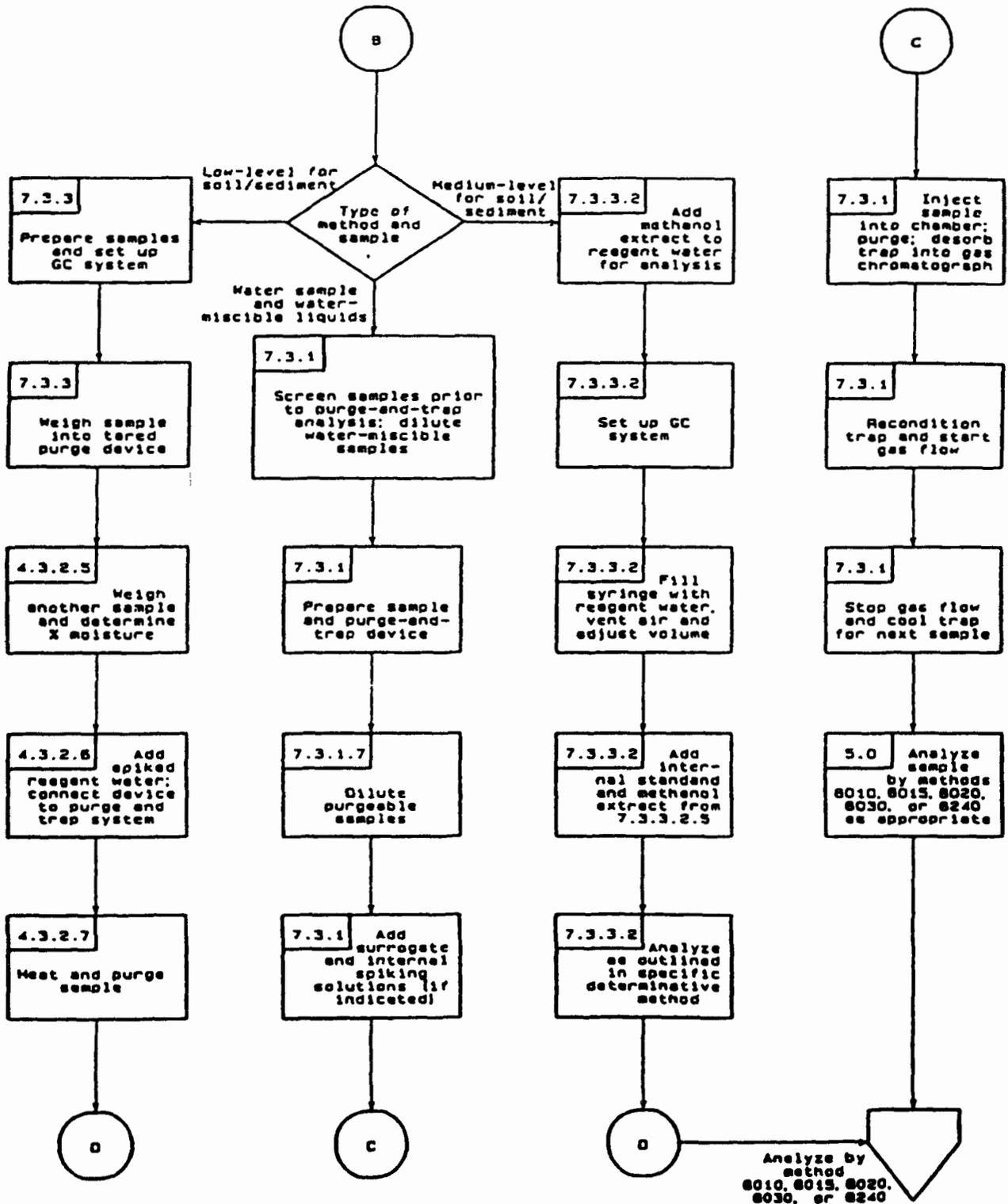
FIGURE 5.
PURGE-AND-TRAP SYSTEM, DESORB MODE,
FOR METHODS 8010, 8020, AND 8030



METHOD 5030
PURGE-AND-TRAP



METHOD 5030
(Continued)



METHOD 6010

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements including metals in solution. The method is applicable to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Methods 3005-3050).

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 8.5.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements.

TABLE 1.
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength ^a (nm)	Estimated Limit ^b (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

^aThe wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.

^bThe estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

^cHighly dependent on operating conditions and plasma position.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multielement instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

TABLE 2.
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM
INTERFERENCE AT THE 100-mg/L LEVEL

Analyte	Wavelength (nm)	Interferent a,b									
		Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

^aDashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L	Mg - 1000 mg/L
Ca - 1000 mg/L	Mn - 200 mg/L
Cr - 200 mg/L	Tl - 200 mg/L
Cu - 200 mg/L	V - 200 mg/L
Fe - 1000 mg/L	

^bThe figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator.

4.1.3 Argon gas supply - Welding grade or better.

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where coordination factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter.

5.1.3 Nitric acid (conc), HNO₃.

5.1.4 Nitric acid (1:1), HNO₃. Add 500 mL concentrated HNO₃ to 400 mL water and dilute to 1 liter.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)} \times \text{mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 100 ug Al: Dissolve 0.10 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO₃ in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1:1) HCl and dilute to 1,000 mL with water.

5.3.2 Antimony solution, stock, 1 mL = 100 ug Sb: Dissolve 0.27 g K(SbO)C₄H₄O₆ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to 1,000 mL with water.

5.3.3 Arsenic solution, stock, 1 mL = 100 ug As: Dissolve 0.13 g of As₂O₃ (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.3.4 Barium solution, stock, 1 mL = 100 ug Ba: Dissolve 0.15 g BaCl₂ (mole fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with water.

5.3.5 Beryllium solution, stock, 1 mL = 100 ug Be: Do not dry. Dissolve 1.97 g BeSO₄·4H₂O (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO₃, and dilute to 1,000 mL with water.

5.3.6 Cadmium solution, stock, 1 mL = 100 ug Cd: Dissolve 0.11 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.3.7 Calcium solution, stock, 1 mL = 100 ug Ca: Suspend 0.25 g CaCO_3 (mole Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

5.3.8 Chromium solution, stock, 1 mL = 100 ug Cr: Dissolve 0.19 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with water.

5.3.9 Cobalt solution, stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with water.

5.3.10 Copper solution, stock, 1 mL = 100 ug Cu: Dissolve 0.13 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3 . Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with water.

5.3.11 Iron solution, stock, 1 mL = 100 ug Fe: Dissolve 0.14 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3 . Cool, add an additional 5.0 mL of concentrated HNO_3 , and dilute to 1,000 mL with water.

5.3.12 Lead solution, stock, 1 mL = 100 ug Pb: Dissolve 0.16 g $\text{Pb}(\text{NO}_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10 mL (1:1) HNO_3 and dilute to 1,000 mL with water.

5.3.13 Lithium solution, stock, 1 mL = 100 ug Li: Dissolve 0.5324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to 1,000 mL with water.

5.3.14 Magnesium solution, stock, 1 mL = 100 ug Mg: Dissolve 0.17 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3 . Add 10.0 mL (1:1) concentrated HNO_3 and dilute to 1,000 mL with water.

5.3.15 Manganese solution, stock, 1 mL = 100 ug Mn: Dissolve 0.1000 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to 1,000 mL with water.

5.3.16 Molybdenum solution, stock, 1 mL = 100 ug Mo: Dissolve 0.20 g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to 1,000 mL with water.

5.3.17 Nickel solution, stock, 1 mL = 100 ug Ni: Dissolve 0.1000 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO₃, cool, and dilute to 1,000 mL with water.

5.3.18 Phosphate solution, stock, 1 mL = 100 ug P: Dissolve 0.4393 g anhydrous KH₂PO₄ (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to 1,000 mL.

5.3.19 Potassium solution, stock, 1 mL = 100 ug K: Dissolve 0.19 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water and dilute to 1,000 mL.

5.3.20 Selenium solution, stock, 1 mL = 100 ug Se: Do not dry. Dissolve 0.17 g H₂SeO₃ (mole fraction Se = 0.6123), weighed accurately to at least four significant figures, in water and dilute to 1,000 mL.

5.3.21 Silver solution, stock, 1 mL = 100 ug Ag: Dissolve 0.16 g AgNO₃ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO₃. Dilute to 1,000 mL with water.

5.3.22 Sodium solution, stock, 1 mL = 100 ug Na: Dissolve 0.25 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.3.23 Strontium solution, stock, 1 mL = 100 ug Sr: Dissolve 0.2415 g of strontium nitrate (Sr(NO₃)₂) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to 1000 mL with water.

5.3.24 Thallium solution, stock, 1 mL = 100 ug Tl: Dissolve 0.13 g TlNO₃ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.3.25 Vanadium solution, stock, 1 mL = 100 ug V: Dissolve 0.23 g NH₄O₃ (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO₃. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.3.26 Zinc solution, stock, 1 mL = 100 ug Zn: Dissolve 0.12 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO₃. Add 10.0 mL concentrated HNO₃ and dilute to 1,000 mL with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add 2 mL (1:1) HNO₃ and 10 mL of (1:1) HCl and dilute to 100 mL with water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral

interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Step 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3.
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni, Li, and Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by diluting 2 mL of (1:1) HNO₃ and 10 mL of (1:1) HCl to 100 mL with water. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The reagent blank must contain all the reagents and in the same volumes as used in the processing of the samples. The reagent blank

must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.2.1 for use).

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Inorganic Analytes, Steps 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of all matrices is always necessary because of the complexity and variability of sample matrices. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005-3050).

7.2 Set up the instrument with proper operating parameters established in Step 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.)

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 minute (Step 5.5.1) before the analysis of each sample (see Note to Step

7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in ug/L with up to three significant figures.

8.0 QUALITY CONTROL

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

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

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

8.4 Analyze one replicate sample for every 20 samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within $\pm 10\%$ of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Matrix spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

8.6.1 Check instrument calibration using a calibration blank and two appropriate standards.

8.6.2 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.2.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.2.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.3 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample (Step 5.7). Results should be within $\pm 20\%$ of the true value obtained in Step 8.6.2.1.

8.6.4 Spiked replicate samples are to be analyzed at a frequency of 20%.

8.6.4.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.

D_1 = first sample value.

D_2 = second sample value (replicate).

(A control limit of $\pm 20\%$ for RPD shall be used for sample values greater than 10 times the instrument detection limit.)

8.6.4.2 The spiked replicate sample recovery is to be within $\pm 20\%$ of the actual value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was $9 \pm 2\%$. The mean percent recovery of spiked elements for all wastes was $93 \pm 6\%$. Spike levels ranged

from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

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TABLE 4.
ICP PRECISION AND ACCURACY DATA^a

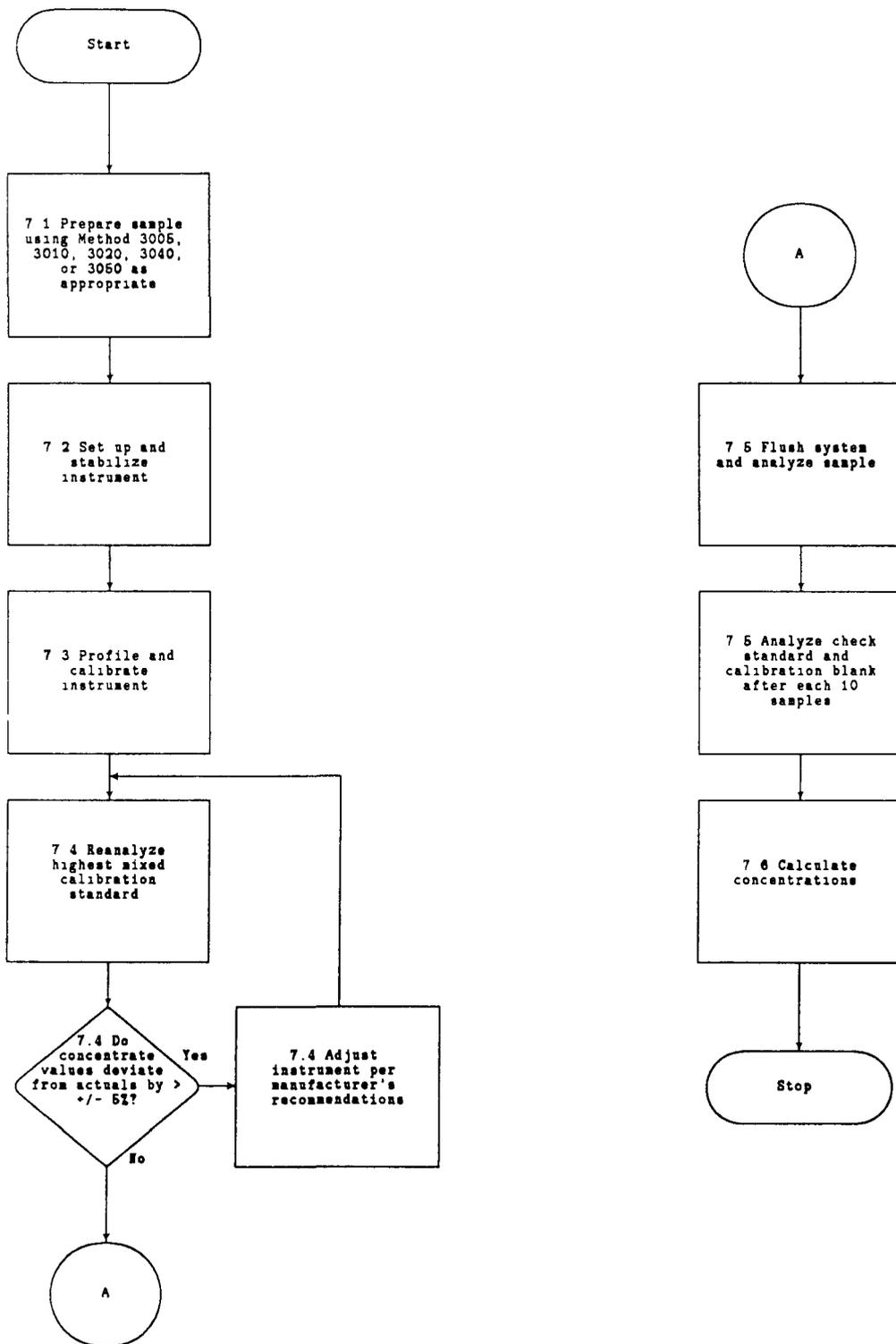
Element	Sample No. 1			Sample No. 2			Sample No. 3		
	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD ^b (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD ^b (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD ^b (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se ^c	40	32	21.9	6	8.5	42	10	8.5	8.3

^aNot all elements were analyzed by all laboratories.

^bSD = standard deviation.

^cResults for Se are from two laboratories.

METHOD 6010
INDUCTIVELY COUPLED ATOMIC EMISSION SPECTROSCOPY



METHOD 6020

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is a technique which is applicable to $\mu\text{g/L}$ concentrations of a large number of elements in water and wastes after appropriate sample preparation steps are taken [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No further digestion is required prior to analysis for dissolved elements. Acid-digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 Elements for which Method 6020 has shown acceptable performance in a multi-laboratory study are listed in TABLE 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. Other elements may be added to Table 1 as more information becomes available. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges for these elements will vary with the matrices, instrumentation, and operating conditions.

1.3 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and the correction of spectral, chemical, and physical interferences in ICP-MS.

1.4 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Tb , ^{165}Ho , and ^{209}Bi . The lithium internal standard should have an enriched abundance of ^6Li , so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of a water-

cooled interface, into a quadrupole mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include ArCl^+ ions on the ^{75}As signal and MoO^+ on the cadmium isotopes. Since the ^{35}Cl natural abundance of 75.8 percent is 3.13 times the ^{37}Cl abundance of 24.2 percent, the chloride corrections can be calculated as follows (where the $^{38}\text{Ar}^{37}\text{Cl}^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}\text{Ar}^{35}\text{Cl}^+$ signal):

corrected arsenic signal = (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.53) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z),

Similarly,

corrected cadmium signal = (m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

The above equations are based upon the constancy of the isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [5] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant.

This type of correction has been reported [5] for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [6]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been recommended [7] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [8]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to 1 amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver above 300 $\mu\text{g/L}$ require 1% (v/v) HCl for

stability. If HCl is added as a stabilizer, then corrections for the chloride molecular-ion interferences must be applied to all data generated.

5.2 Reagent water: Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100 μg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3 . Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100 μg Ho: Dissolve 0.1757 g $\text{Ho}_2(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$ in 10 mL reagent water and 10 mL HNO_3 . After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100 μg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3 . Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100 μg ^6Li : Dissolve 0.6312 g 95-atom-% ^6Li , Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3 . After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100 μg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(\text{NH}_4)_3\text{RhCl}_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100 μg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3 . Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100 μg Tb: Dissolve 0.1828 g $\text{Tb}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 10 mL (1+1) HNO_3 . After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100 μg Y: Dissolve 0.2316 g $\text{Y}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ in 10 mL (1+1) HNO_3 . Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100 μ g Ti: Dissolve 0.4133 g $(\text{NH}_4)_2\text{TiF}_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 μ g Mo: Dissolve 0.2043 g $(\text{NH}_4)_2\text{MoO}_4$ in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions -- Dilute the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^6Li , ^{45}Sc , ^{89}Y , ^{103}Rh , ^{115}In , ^{159}Te , ^{169}Ho , and ^{209}Bi . Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control sample (see Section 5.8) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The reagent blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of 1 percent HNO_3 (v/v) in reagent water along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes.

5.5.2 The reagent blank must contain all the reagents in the same volumes as used in processing the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solutions used for analysis.

5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration ranges.

5.7 The interference check solution(s) (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}\text{Cl}^{16}\text{O}^+$ on $^{51}\text{V}^+$ and $^{40}\text{Ar}^{35}\text{Cl}^+$ on $^{75}\text{As}^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.7.1 The final concentrations of elements in ICS A and ICS AB are shown in Table 2. These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.7.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 2.498 g CaCO_3 (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3 , and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3 . After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.7.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4 , 6.373 g 96% H_2SO_4 , 40.024 g 37% HCl, and 10.664 g citric acid $\text{C}_6\text{O}_7\text{H}_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.7.1.3 Mixed ICS solution III may be prepared by adding 5 mL each of 100 $\mu\text{g}/\text{mL}$ arsenic stock solution, chromium stock solution, copper stock solution, manganese stock solution, selenium stock solution, silver stock solution, and zinc stock solution, 10 mL each of 100 $\mu\text{g}/\text{mL}$ cobalt stock solution, nickel stock solution, and vanadium stock solution, and 2.5 mL of 100 $\mu\text{g}/\text{mL}$ cadmium stock solution. Dilute to 100 mL with 2% HNO_3 .

5.7.1.4 Working ICS Solutions

5.7.1.4.1 ICS A may be prepared by adding 50 mL of mixed ICS solution I (5.7.1.1), 10 mL each of 100 $\mu\text{g}/\text{mL}$ titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 25 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.7.1.4.2 ICS AB may be prepared by adding 50 mL of mixed ICS solution I (5.7.1.1), 10 mL each of 100 $\mu\text{g}/\text{mL}$ titanium stock solution (5.3.9) and molybdenum stock solution

(5.3.10), 25 mL of mixed ICS solution II (5.7.1.2), and 2 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. ICS solution AB must be prepared fresh weekly.

5.8 The quality control sample is the initial calibration verification solution, which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or Teflon containers are recommended for use in Method 6020.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g. Methods 3005 - 3050).

7.2 Initiate appropriate operating configuration of the instrument computer.

7.3 Set up the instrument with the proper operating parameters.

7.4 Operating conditions: In general, the analyst should follow the instructions provided by the instrument manufacturer. The following is a suggested listing of operating conditions which may be useful.

	Perkin-Elmer Sciex <u>Elan 500</u>	<u>VG Plasmaquad</u>
Plasma Gas (lpm)	12	13
Aux. Gas (lpm)	1.2	0.65
Neb. Gas (lpm)	0.95	0.69
Forward power (kW)	1.2	1.30
Reflected power (W)	< 5	< 5
Sampling Height (mm above load coil)	18	12

Note: Addition of nitrogen to the plasma argon has been reported to decrease many molecular interferences [9].

Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (such as 100 $\mu\text{g/L}$ Li, Co, In, and Tl) at least four times with relative standard deviations of less than 10% for the analytes contained in the tuning solution.

Note: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration exceeds a difference of more than 0.1 amu from the actual value, then the mass calibration must be adjusted to the correct values. The resolution must also be verified to be less than 1.0 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest for the isotopes shown in Table 3 using the calibration blank and at least a single standard according to the manufacturer's recommended procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of the multiple integrations for both standardization and sample analysis.

7.7 Some elements (such as Hg, W, and Mo) require extended flushing times which need to be determined for each instrumental system.

7.8 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. These masses must be monitored either simultaneously in a separate scan or at the same time quantification occurs.

7.9 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the initial calibration verification solution (Section 5.8). When measurements exceed $\pm 10\%$ of the accepted value the analysis must be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Any samples analyzed under an out-of-control calibration must be reanalyzed.

7.10 Flush the system with the rinse blank solution (5.5.3) for at least 30 seconds before the analysis of each sample (see Section 7.7). Aspirate each sample for at least 30 seconds before collecting data. Analyze the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples.

7.11 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope.

7.12 Calculations: The quantitative values shall be reported in units of micrograms per liter ($\mu\text{g/L}$) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.12.1 Results for solids must be reported on a dry-weight basis as follows:

- (1) A separate determination of percent solids must be performed.
- (2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\% \text{ Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal standard normalization, and the summation of signals at 206, 207, and 208 m/z for lead to compensate for any differences in the abundances of these isotopes between samples and standards.

8.0 QUALITY CONTROL

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

8.2 Instrument Detection Limits (IDL's) (in $\mu\text{g/L}$) can be estimated by multiplying by three the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x-25x IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDL's must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standard. This procedure must be repeated until the internal standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration blank solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are below the levels that show an effect on the analyte level, uncorrected equations may be used provided all QC criteria are met. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When corrected equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use established isotopic response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) are acceptable corrections for use in Method 6020.

8.5 Serial dilution: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of 100 above the instrumental detection limit), an analysis of a fivefold dilution must agree within $\pm 10\%$ of the original determination. If not, an interference effect must be suspected. One serial dilution must be analyzed for each twenty samples or less of each matrix in a batch.

8.6 Matrix spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value. The spike addition should produce a minimum signal level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure can usually

compensate for this effect. See Section 8.5.3 of Method 6010 for information on standard additions.

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument standardization by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.8 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within $\pm 10\%$ of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed at no additional cost to the government.

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and affected samples must be reanalyzed.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this by analyzing the interference check solutions A and AB

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$\text{RPD} = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.

D₁ = first sample value.

D₂ = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 5 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 6.

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TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #	Estimated Detection Limit ($\mu\text{g/L}$)
Aluminum	7429-90-5	0.1
Antimony	7440-36-0	0.02
Arsenic	7440-38-2	0.4
Barium	7440-39-3	0.02
Beryllium	7440-41-7	0.1
Cadmium	7440-43-9	0.07
Chromium	7440-47-3	0.02
Cobalt	7440-48-4	0.01
Copper	7440-50-8	0.03
Lead	7439-92-1	0.02
Manganese	7439-96-5	0.04
Nickel	7440-02-0	0.03
Silver	7440-22-4	0.04
Thallium	7440-28-0	0.05
Zinc	7440-66-6	0.08

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS.

Interference component	Solution A Concentration (mg/L)	Solution AB Concentration (mg/L)
Al	500.0	500.0
Ca	500.0	500.0
Fe	500.0	500.0
Mg	500.0	500.0
Na	500.0	500.0
P	500.0	500.0
K	500.0	500.0
S	500.0	500.0
C	1000.0	1000.0
Cl	3600.0	3600.0
Mo	10.0	10.0
Ti	10.0	10.0
As	0.0	0.100
Cd	0.0	0.050
Cr	0.0	0.100
Co	0.0	0.200
Cu	0.0	0.100
Mn	0.0	0.100
Ni	0.0	0.200
Ag	0.0	0.100
Zn	0.0	0.100

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
<u>27</u>	Aluminum
<u>121</u> , 123	Antimony
<u>75</u>	Arsenic
138, 137, 136, <u>135</u> , 134	Barium
<u>9</u>	Beryllium
209	Bismuth (IS)
<u>114</u> , 112, <u>111</u> , 110, 113, 116, 106	Cadmium
42, 43, <u>44</u> , 46, 48	Calcium (I)
35, 37, (77, 82) ^a	Chlorine (I)
<u>52</u> , <u>53</u> , <u>50</u> , 54	Chromium
<u>59</u>	Cobalt
<u>63</u> , <u>65</u>	Copper
165	Holmium (IS)
<u>115</u> , 113	Indium (IS)
<u>56</u> , <u>54</u> , <u>57</u> , 58	Iron (I)
139	Lanthanum (I)
<u>208</u> , <u>207</u> , <u>206</u> , 204	Lead
<u>6^b</u> , 7	Lithium (IS)
24, <u>25</u> , <u>26</u>	Magnesium (I)
<u>55</u>	Manganese
98, 96, 92, <u>97</u> , 94, (108) ^a	Molybdenum (I)
58, <u>60</u> , 62, <u>61</u> , 64	Nickel
<u>39</u>	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
<u>107</u> , <u>109</u>	Silver
<u>23</u>	Sodium (I)
159	Terbium (IS)
<u>205</u> , 203	Thallium
120, <u>118</u>	Tin (I)
89	Yttrium (IS)
64, <u>66</u> , <u>68</u> , <u>67</u> , 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferences (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. ^a These masses are also useful for interference correction (Section 3.2). ^b Internal standard must be enriched in the ⁶Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. SPIKING LEVELS FOR ICP-MS ANALYSIS ($\mu\text{g/L}$)

Element	Water	Soil
Aluminum	500	*
Antimony	100	100
Arsenic	100	100
Barium	200	200
Beryllium	50	50
Cadmium	50	50
Chromium	50	50
Cobalt	100	100
Copper	50	50
Lead	50	50
Manganese	50	50
Nickel	100	100
Silver	50	50
Thallium	50	50
Vanadium	100	100
Zinc	100	100

* No spike required.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability ^a Range	%RSD Range	N ^b	S ^c
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

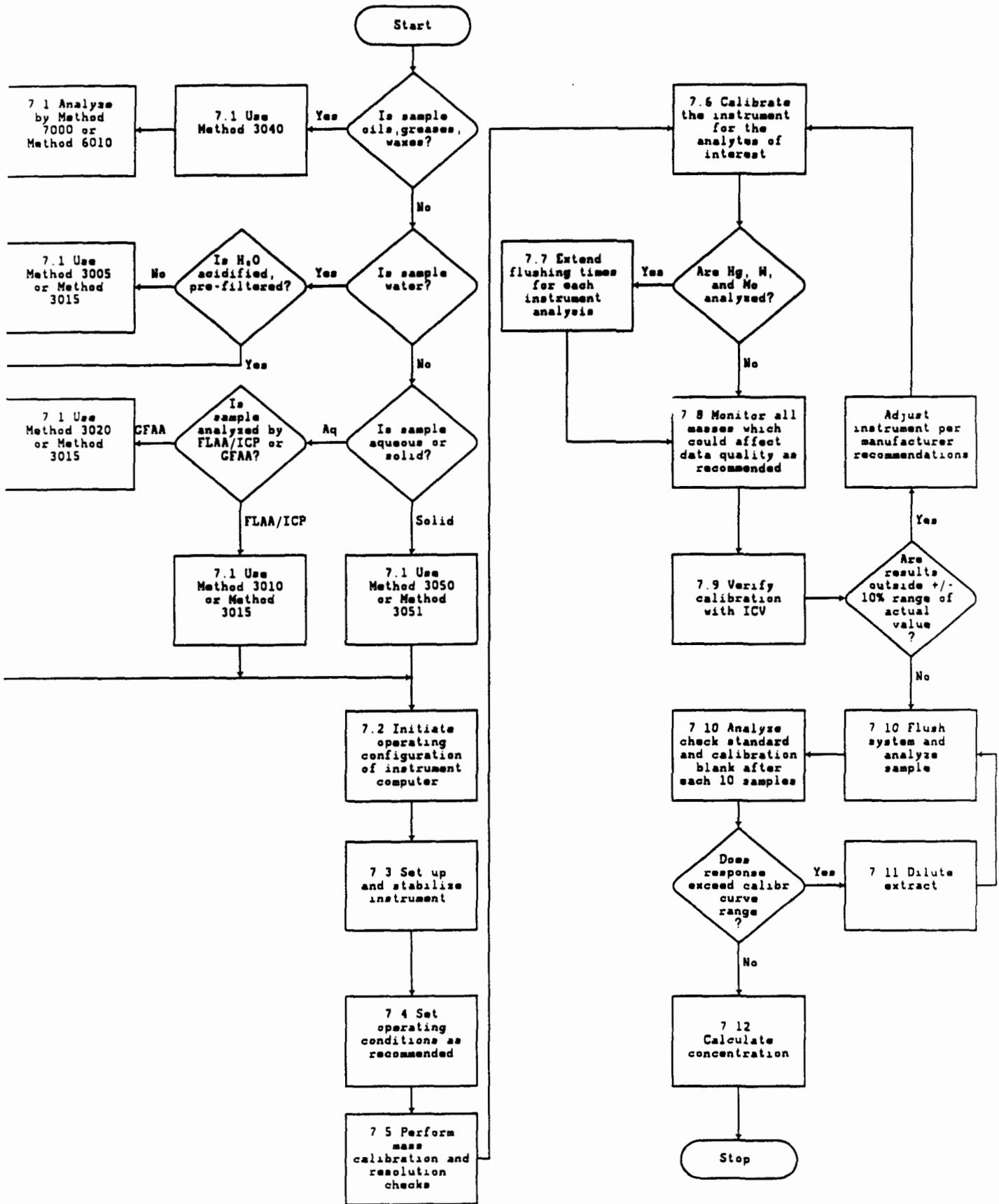
^a Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. ^b N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). ^c S is the number of samples with results greater than the limit of quantitation. ^d No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 6. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability ^a Range	%RSD Range	N ^b	S ^c
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

^a Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. ^b N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). ^c S is the number of samples with results greater than the limit of quantitation. ^d No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020
INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY



METHOD 7000

ATOMIC ABSORPTION METHODS

1.0 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 water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward 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. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. 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 ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and 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.

Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because 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.

2.4 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 is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that 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. 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 or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 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 when 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 phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 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. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 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 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, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.
2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. 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.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 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 analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources 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 Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and Type II water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both

analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Strip-chart recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 μ L as required. Pipet tips should be checked as a possible source of contamination prior to their use.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and Type II water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently

high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water.

5.4 Hydrochloric acid (1:1), HCl . Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water.

5.5 Fuel and oxidant - Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - 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 absorbance of 0.0 to 0.7. 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 a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. 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. 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.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and 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. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods.

7.2 Direct aspiration (flame) procedure

7.2.1 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 a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp 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 current according to the manufacturer'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. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument 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 is run.

7.3 Furnace procedure

7.3.1 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 instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, 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. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic

graphite is used, the rate of atomization, and furnace design. 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 during the series of determinations.

7.3.4 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.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. 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 will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value in ug/L from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \frac{(C + B)}{C}$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations as ug/kg based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

Z = ug/L of metal read from calibration curve or read-out system.

B = Acid blank matrix used for dilution mL.

C = Sample aliquot, mL.

8.0 QUALITY CONTROL

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

8.2 A calibration curve must be prepared each day with a minimum of a reagent blank and three standards, verified by use of at least a reagent blank and one check standard at or near the mid-range. Checks throughout the day must be within 20% of original curve.

8.3 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 mid-range every 10 samples. Checks must be within $\pm 20\%$ of true value.

8.4 At least one spiked matrix and one replicate sample should be run every 20 samples or per analytical batch, whichever is greater. At least one spiked replicate sample should also be run with each matrix type to verify precision of the method.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used (see Step 8.7 below).

8.6 Serial dilution - 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 that the diluted value should be at least 5 times the instrument detection limit. 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 with the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent

that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift.

8.7.1 In the simplest version of this technique is the single addition method, in which two identical aliquots of the sample solution, each of volume V_x , are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s . To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. Equal volumes of the sample are added to a series of standard solutions containing different known quantities of the test analyte, all diluted to the same volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected sample absorbance. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected sample absorbances, respectively. 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 Figure 1.

8.7.3 For the results of this technique to be valid, the following limitations must be taken into consideration:

1. 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 standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. 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.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure ^{a,c} Detection Limit (ug/L)
	Detection Limit (mg/L)	Sensitivity (mg/L)	
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic ^b	0.002	--	1
Barium	0.1	0.4	--
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	--
Iron	0.03	0.12	--
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	--
Mercury ^d	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium ^b	0.002	--	2
Silver	0.01	0.06	--
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	--

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

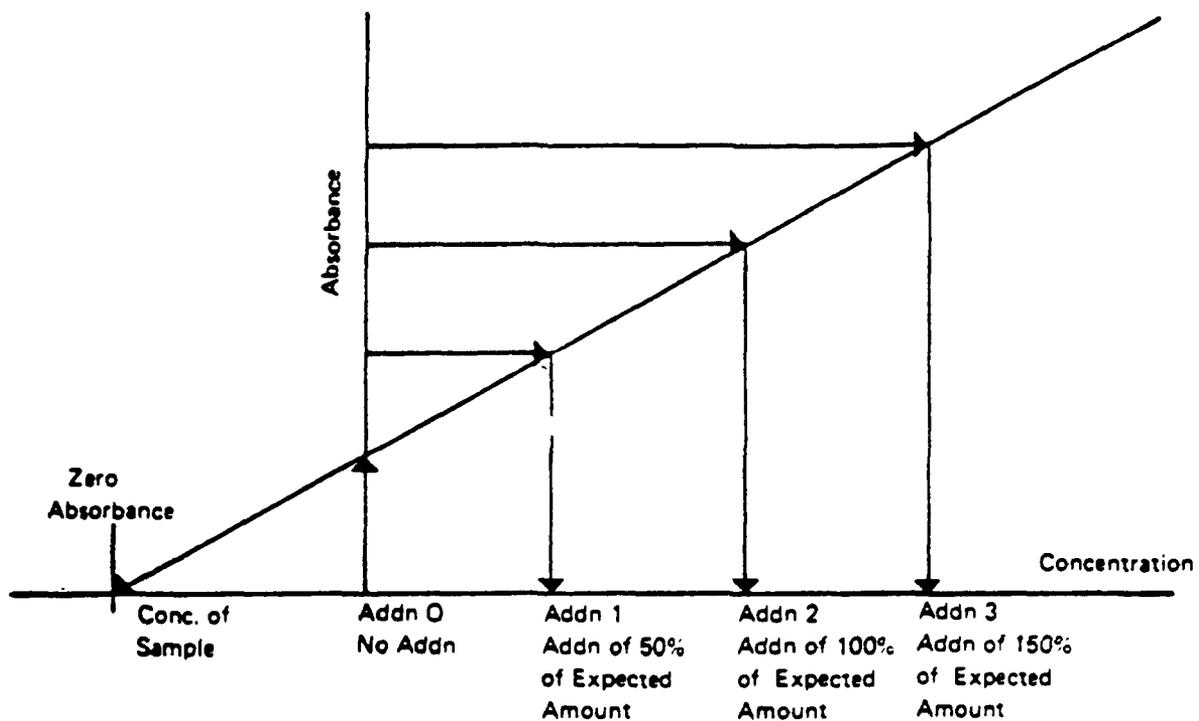
a For furnace sensitivity values, consult instrument operating manual.

b Gaseous hydride method.

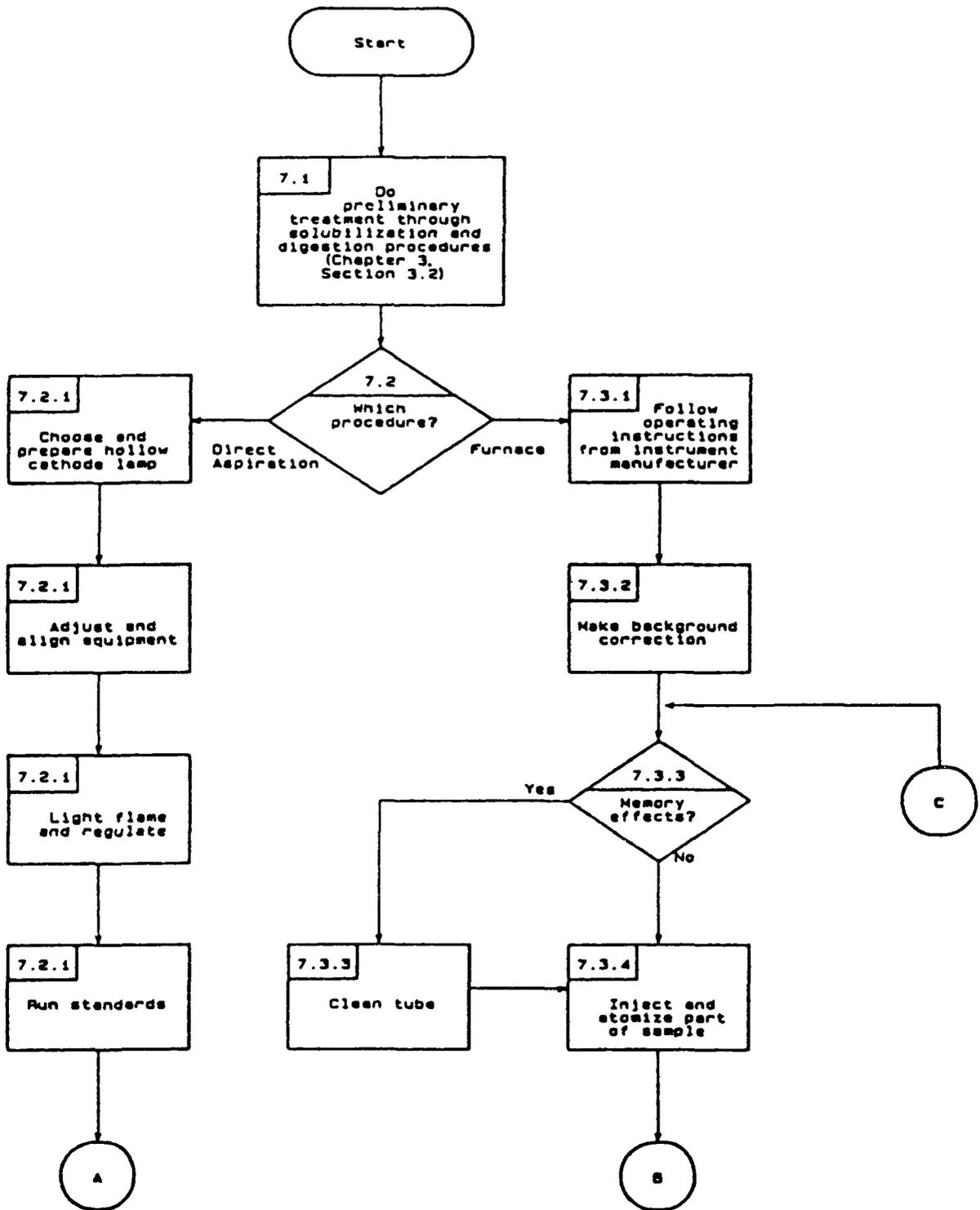
c The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

d Cold vapor technique.

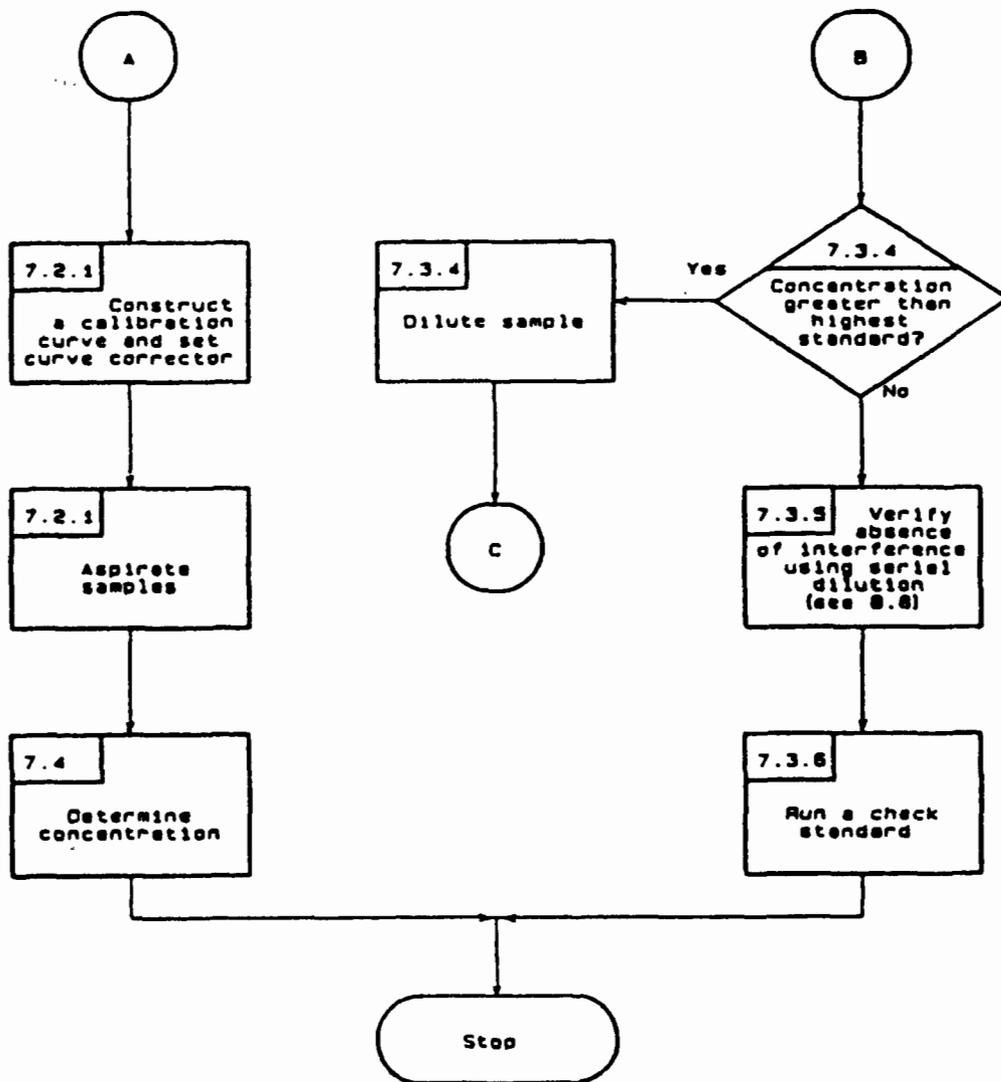
FIGURE 1.
STANDARD ADDITION PLOT



METHOD 7000
ATOMIC ABSORPTION METHODS



METHOD 7000
(Continued)



METHOD 7060A

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive

interferent in the analysis of arsenic, especially using D₂ arc background correction. Zeeman background correction is very useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provision for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 μ L, as required.

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H₂O₂ is <MDL, the acid can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As₂O₃, analytical reagent

grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO₃ and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade Ni(NO₃)₂·6H₂O or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO₃, 30% H₂O₂, and 5% nickel nitrate solution. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% H₂O₂ and sufficient concentrated HNO₃ to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured 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.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

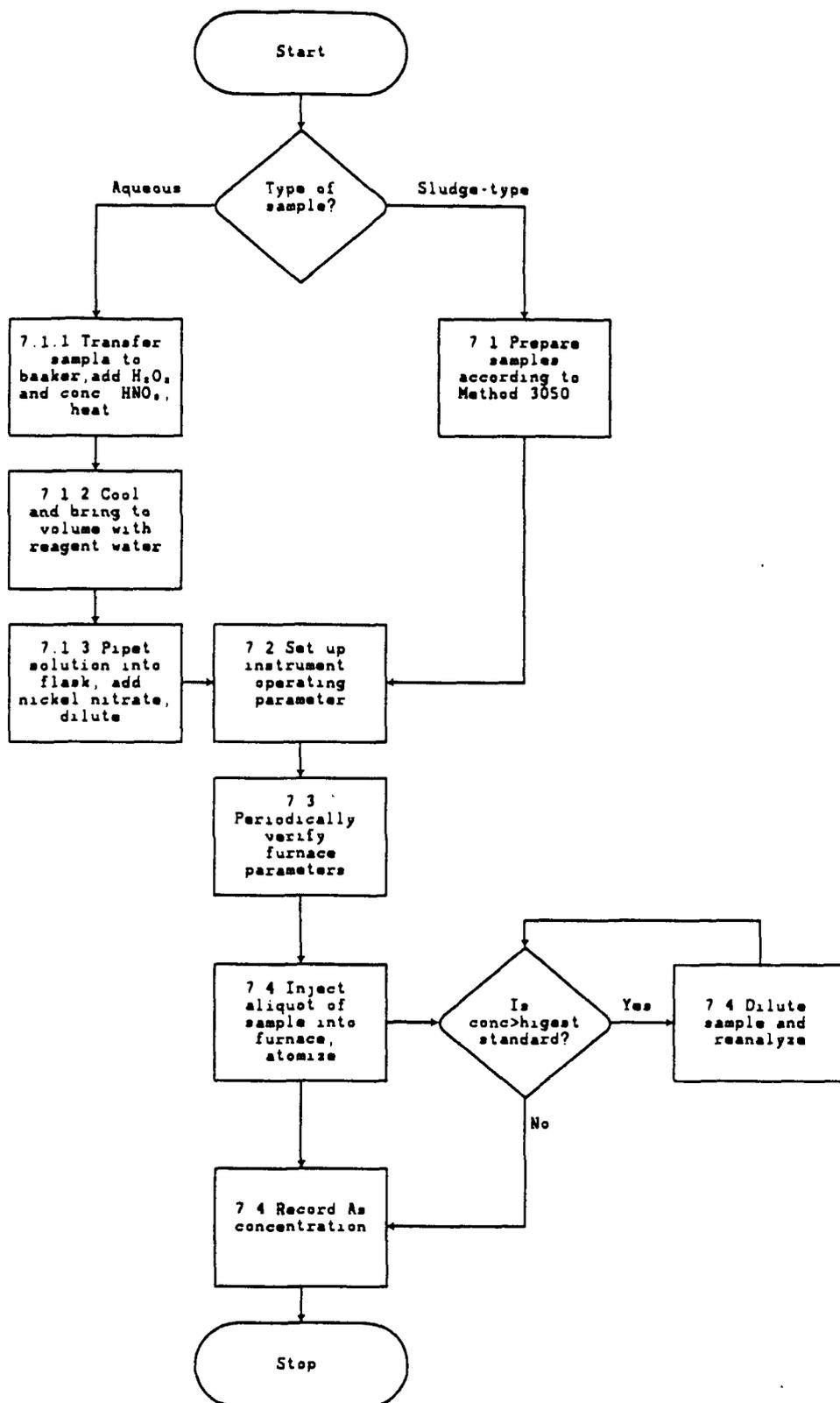
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Dirty soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g ^a
Emission control dust	3050	430, 350 ug/g

Bias of -30 and -28% from expected, respectively.

METHOD 7060A
ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7061

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061 is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO₃) are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker - 100-mL.

4.2 Electric hot plate.

4.3 A commercially available zinc slurry/hydride generator or a generator constructed from the following materials (see Figure 1):

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

4.3.3 Gas inlet-outlet tube - Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer - To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube - 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner - Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3 . Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4 . Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl . Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.6 Diluent - Add 100 mL 18N H₂SO₄ and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g SnCl₂ in 100 mL concentrated HCl.

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As₂O₃ in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO₃ and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO₃/liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO₃/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g. containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of < 2 with nitric acid.

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

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO₃ and 12 mL 18N H₂SO₄. Evaporate the sample in the hood on an electric hot plate until white SO₃ 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 HNO₃. Continue to add additional HNO₃ 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 SO₃ fumes, the digestion is complete. Cool the sample, add about 25 mL water, and again evaporate until SO₃ fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL SnCl₂ 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 dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

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

8.2 Calibration curves must be composed of a minimum of a calibration blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

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

8.5 Verify calibration with an independently prepared quality control reference sample every 10 samples.

8.6 Run one matrix spiked replicate or one replicate sample for every 20 samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process.

8.7 The method of standard additions shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.8 See Section 8.0 of Method 7000 for additional quality control requirements.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

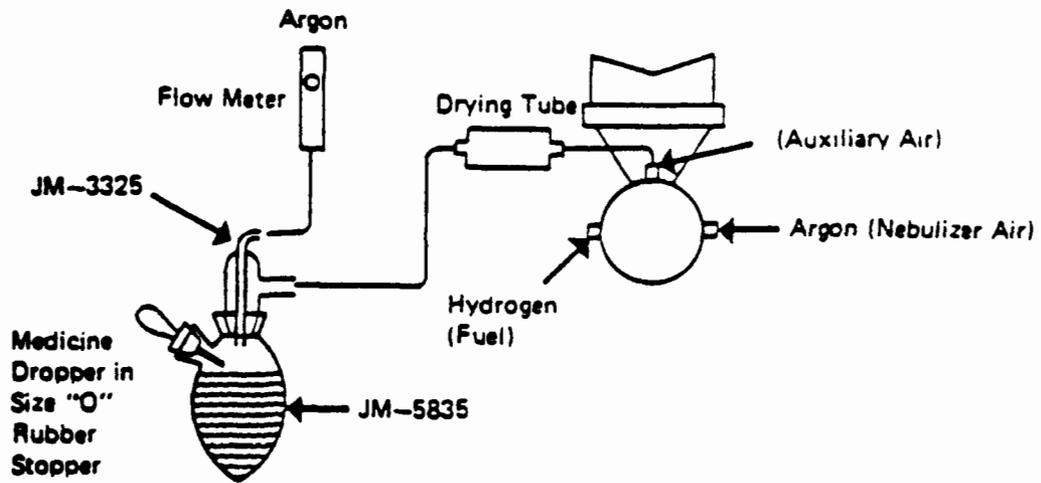
10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

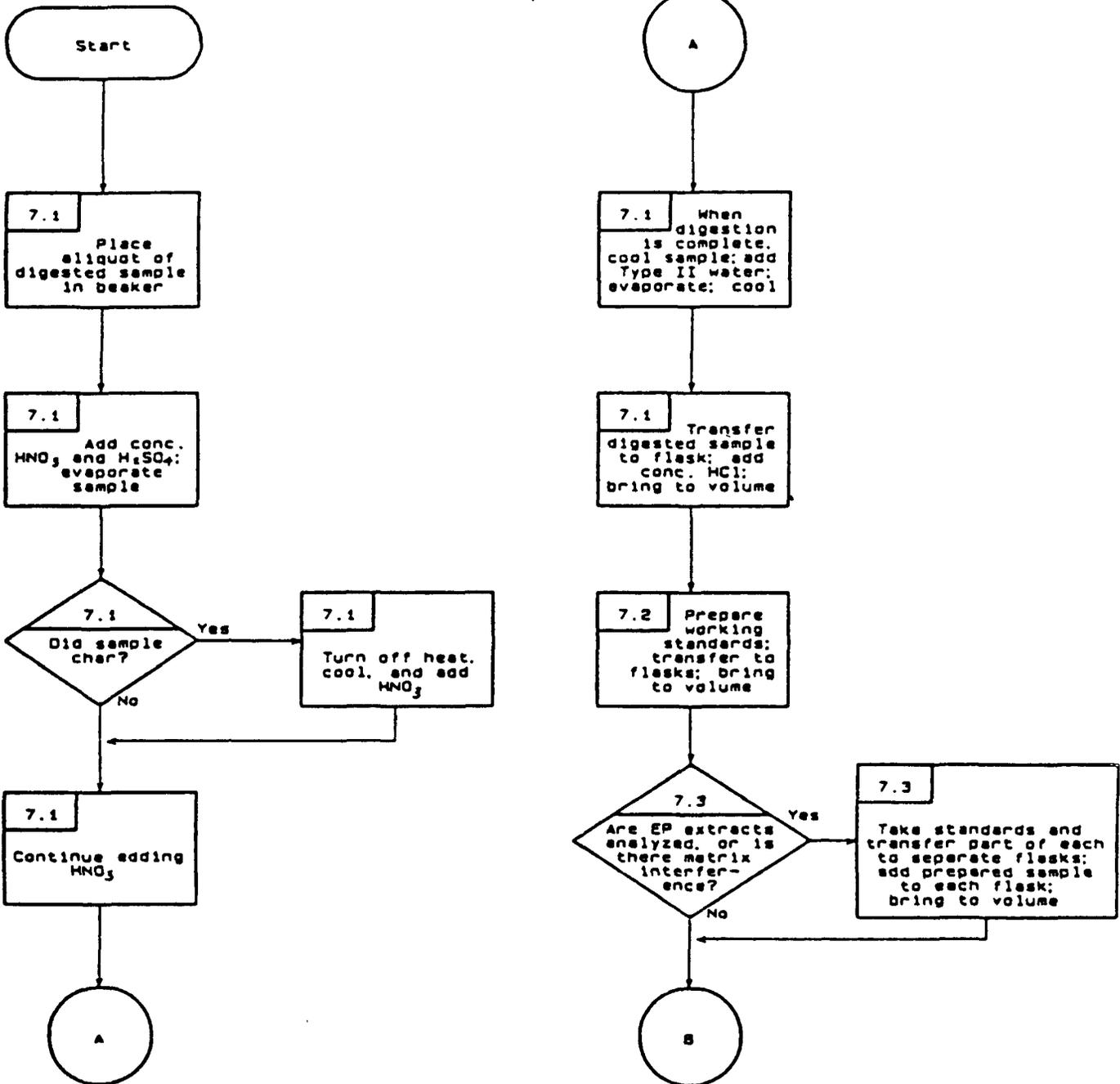
2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

Figure 1.

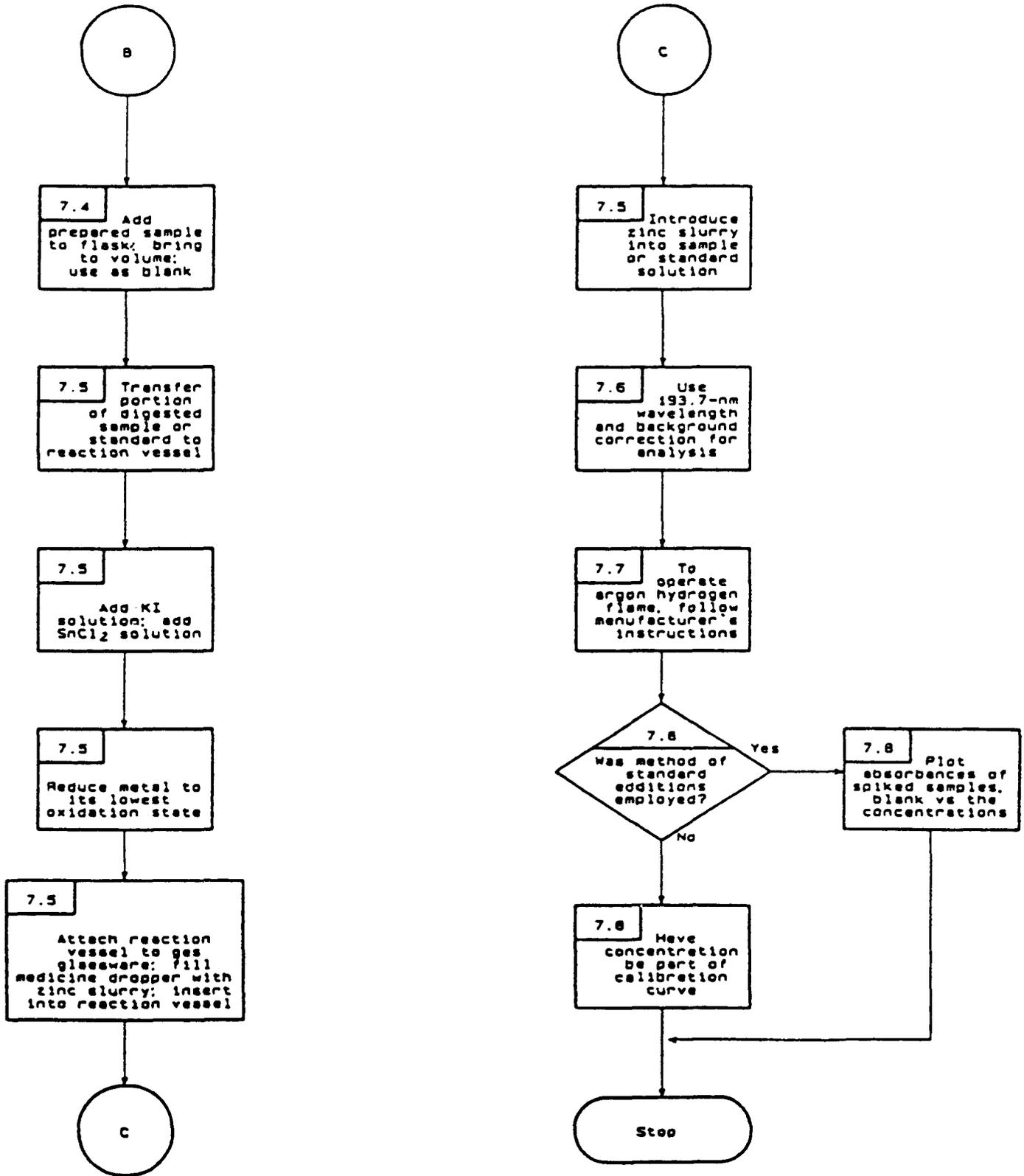
Zinc slurry hydride generator apparatus set-up and AAS sample introduction system.



METHOD 7061
 ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7061
 ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)
 (Continued)



METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 $\mu\text{g}/\text{L}$ to 400 $\mu\text{g}/\text{L}$ concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to 4000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 40% by weight of the interferences before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cystine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into an air-acetylene flame heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 $\mu\text{g}/\text{L}$.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of teflon and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condenser coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C by an air-acetylene flame.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slots is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO₃): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H₂O₂): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

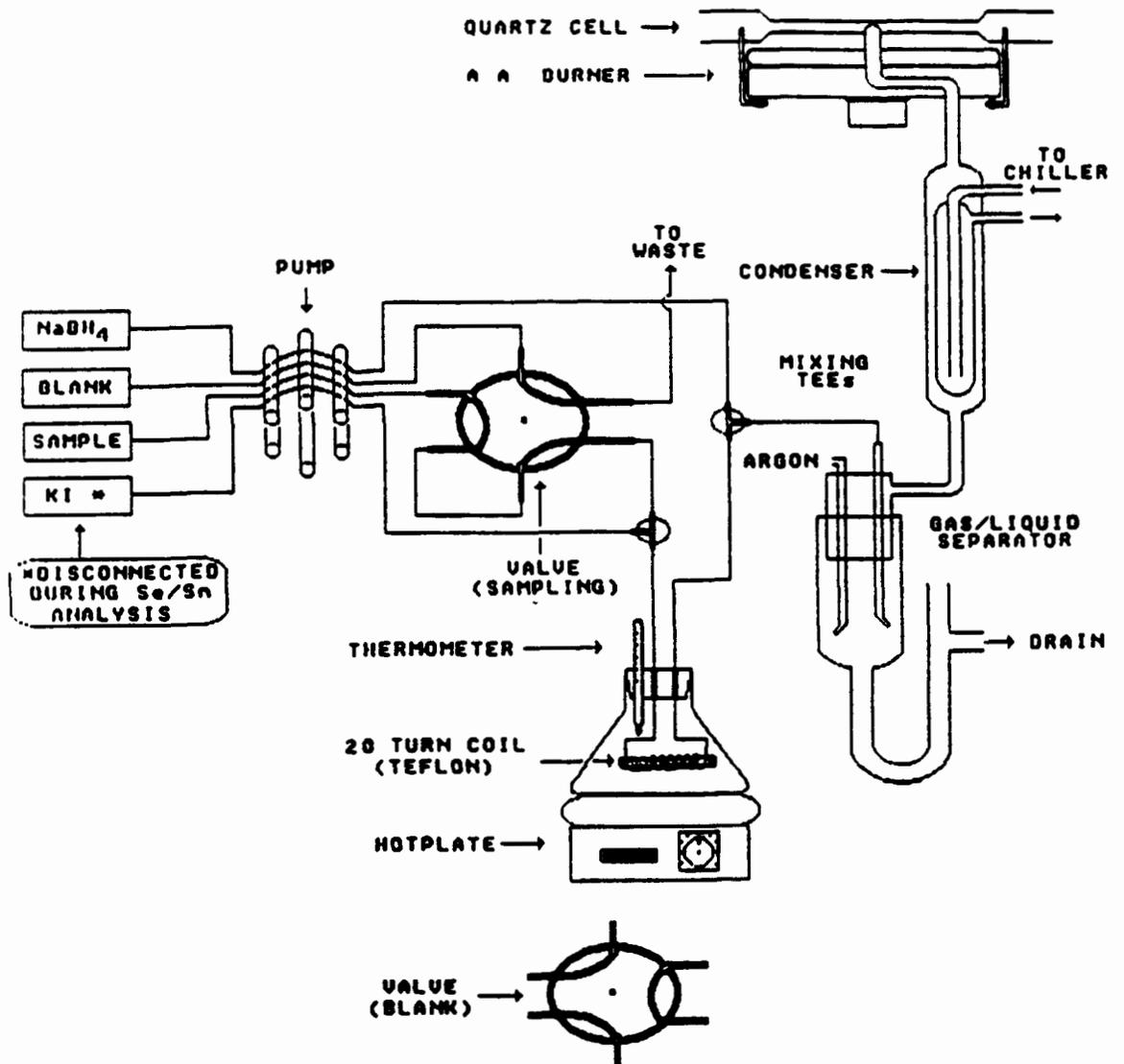


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cystine ($\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride (NaBH_4): A 4% sodium borohydride solution (20 g reagent-grade NaBH_4 plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 Antimony and arsenic stock standard solution (1,000 mg/L): Either procure certified aqueous standards from a supplier (Spex, Inorganic Ventures, or equivalent) and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 Intermediate antimony and arsenic solution: Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 10 μg each of Sb and As).

5.10.3 Standard antimony and arsenic solution: Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter (1 mL = 1 μg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 $\mu\text{g/L}$ or if interferences are expected to exceed 5000 mg/L in the digest.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cystine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cystine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescence is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 μg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA,

use the 217.6-nm wavelength and 0.7-nm slit width without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width without background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

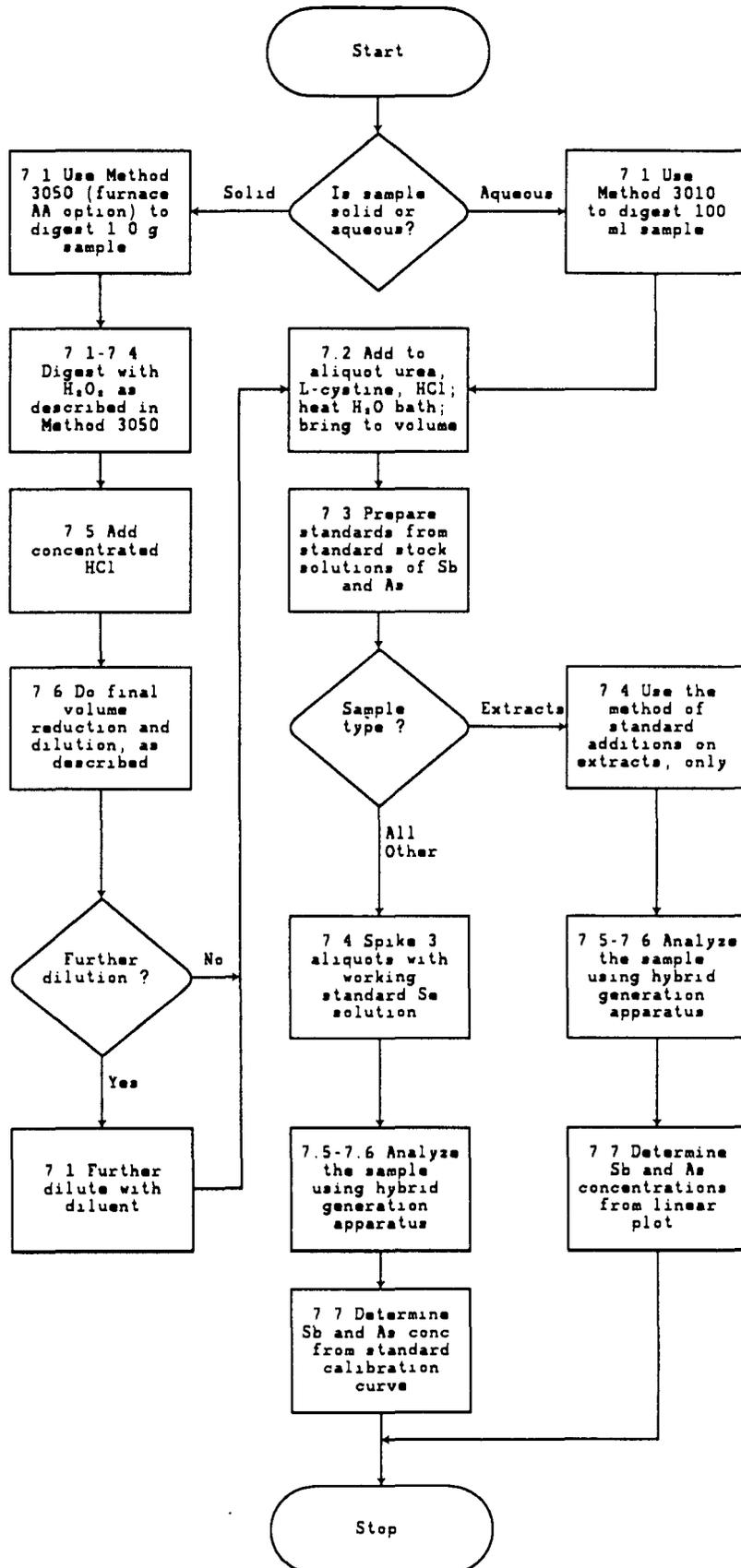
9.0 METHOD PERFORMANCE

9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7062
 ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)



METHOD 7080A

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain a ionization suppressant. Type of suppressant and concentration must be documented.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Barium hollow cathode lamp.

4.2.2 Wavelength: 553.6 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Nitrous oxide.

4.2.5 Type of flame: Fuel rich.

4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) analytical reagent grade in reagent water and dilute to 1

liter (1000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 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 after processing. All calibration standards and samples should contain the ionization suppressant. KCl is detailed in Section 5.2.3.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

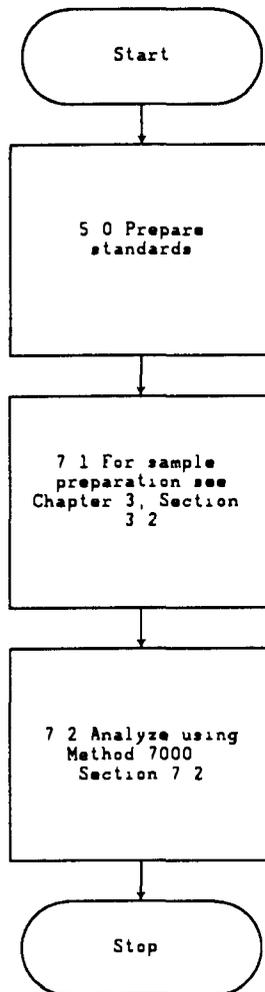
Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of ± 0.043 and ± 0.13 , respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.

METHOD 7080A
BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7131A

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss. Other modifiers may be used as long as it is documented with the type of suppressant and concentration.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 500°C.

4.2.3 Atomizing time and temp: 10 sec at 1900°C.

4.2.4 Purge gas: Argon.

4.2.5 Wavelength: 228.8 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20- μ L injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of 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.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with reagent water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 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 .

5.2.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ (analytical reagent grade), in reagent water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000 .

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

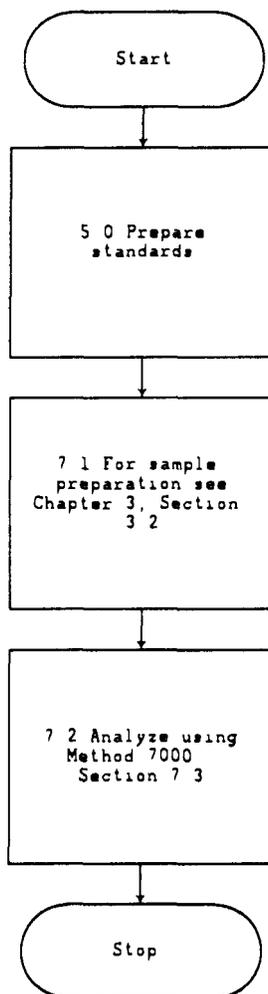
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g ^a
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

^aBias of -3% from expected value.

METHOD 7131A
CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7196

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Step 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment - One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Potassium dichromate stock solution - Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$, in water and dilute to 1 liter (1 mL = 50 ug Cr).

5.4 Potassium dichromate standard solution - Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.5 Sulfuric acid ((10%) (v/v)), H_2SO_4 . Dilute 10 mL of distilled reagent grade or spectrograde quality H_2SO_4 to 100 mL with water.

5.6 Diphenylcarbazide solution - Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.7 Acetone, CH_3COCH_3 . Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hours.

7.0 PROCEDURE

7.1 Color development and measurement - Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5 , dilute to 100 mL with water, and let stand 5 to 10 minutes for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents

except diphenyl semicarbazide should be prepared and used to correct the sample for turbidity (i.e. a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 10 to 200 ug/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. The increase must be ≥ 30 ug Cr(VI)/L. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is

obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Step 8.7).

8.0 QUALITY CONTROL

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

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

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

8.4 Verify calibration with an independently prepared QC reference sample every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every 10 samples. A replicate sample is a sample brought through the whole sample preparation and analytical process.

8.6 The method of standard additions (see Method 7000, Step 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

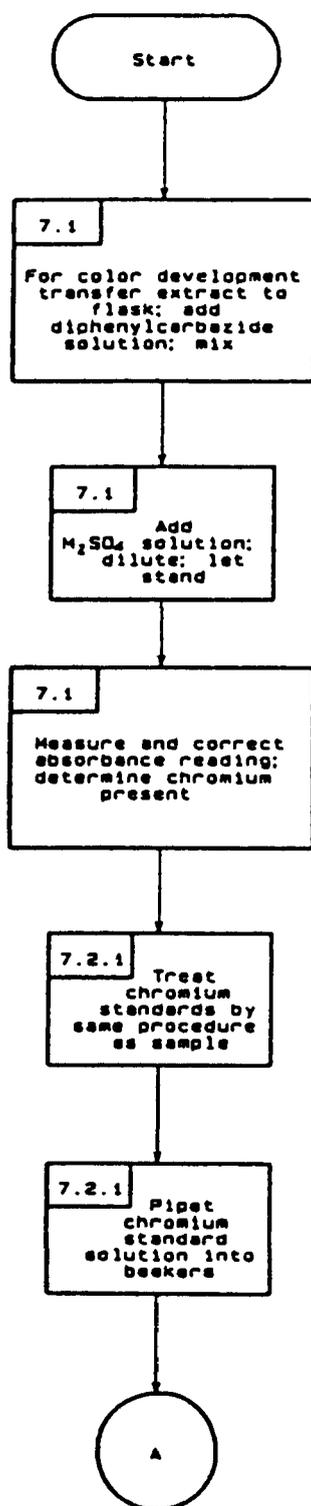
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

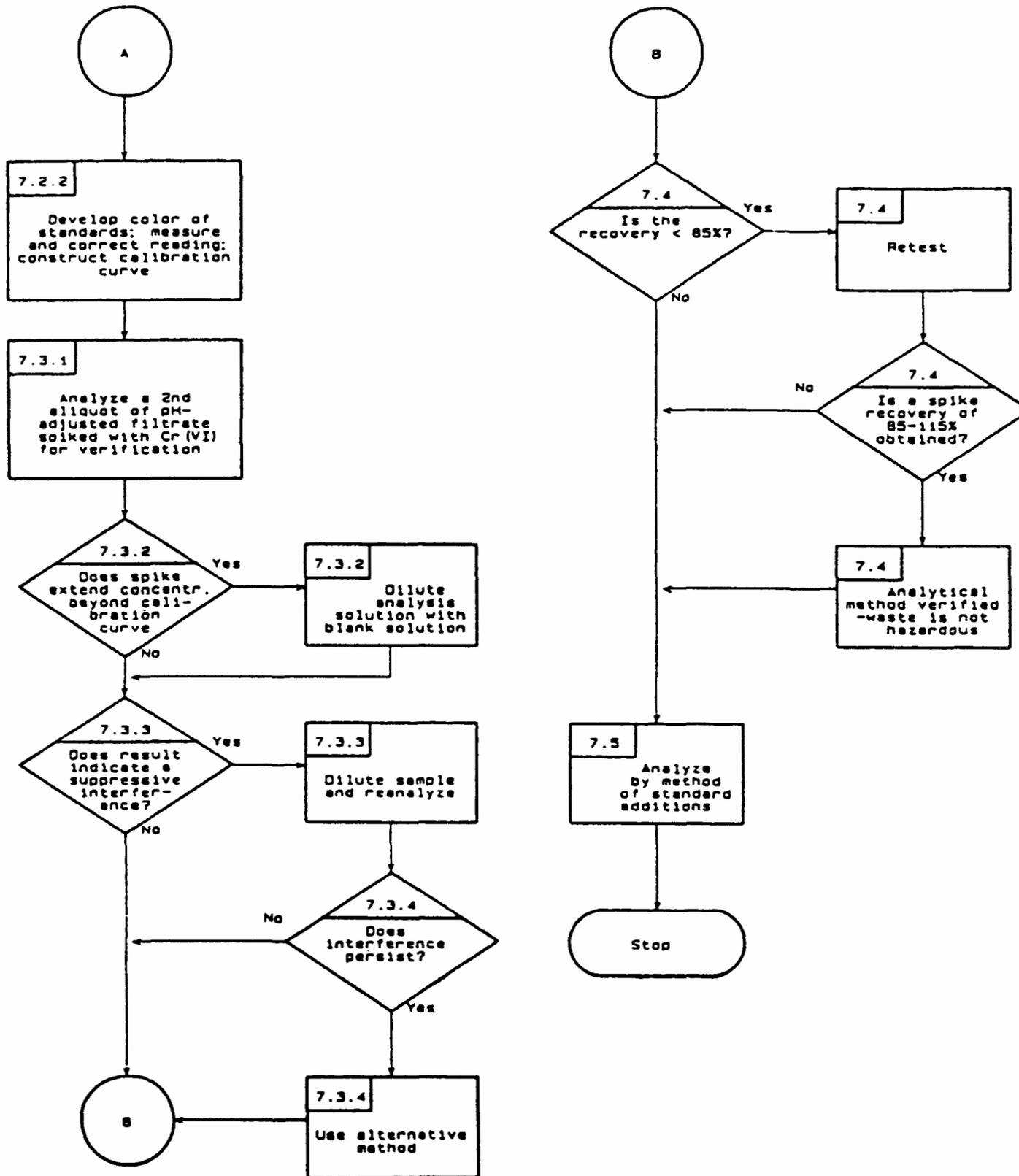
TABLE 1.
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g

METHOD 7196
HEXAVALENT CHROMIUM (COLORIMETRIC)



METHOD 7196
 HEXAVALENT CHROMIUM (COLORIMETRIC)
 (Continued)



METHOD 7430

LITHIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Lithium hollow cathode lamp.

4.2.2 Wavelength: 670.8 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background Correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution: (1.0 mL = 1.0 mg Li). Dissolve 5.324 g lithium carbonate, Li_2CO_3 , in a minimum volume of 1:1 HCl and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 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 as the samples used to prepare the samples and cover the range of expected concentrations in the samples.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-2 mg/L at a wavelength of 670.8 nm.

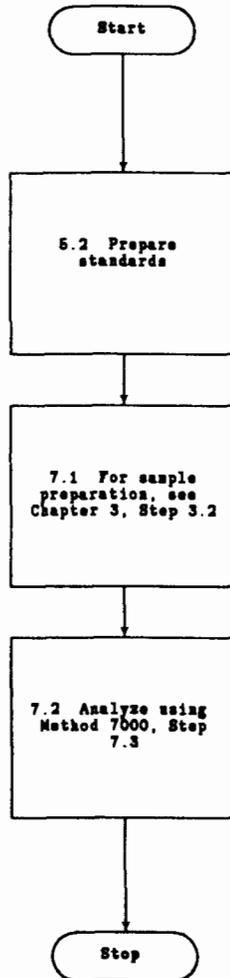
Sensitivity: 0.04 mg/L.

Detection limit: 0.002 mg/L.

10.0 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 16th ed.; Greenberg, A.E.; Trussell, R.R.; Clesceri, L.S., Eds.; American Water Works Association, Water Pollution Control Federation, American Public Health Association: Washington, DC, 1985.

METHOD 7430
LITHIUM (ATOMIC ASORPTION, DIRECT ASIRATION)



METHOD 7470A

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 ; or
2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4 . This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 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 addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Aqueous samples must be acidified to a pH <2 with HNO₃. The suggested maximum holding times for mercury is 28 days.

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

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H₂SO₄ and 2.5 mL of concentrated HNO₃, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H₂SO₄ and 2.5 mL of concentrated HNO₃ to each bottle. Add 15 mL of KMnO₄ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass

valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

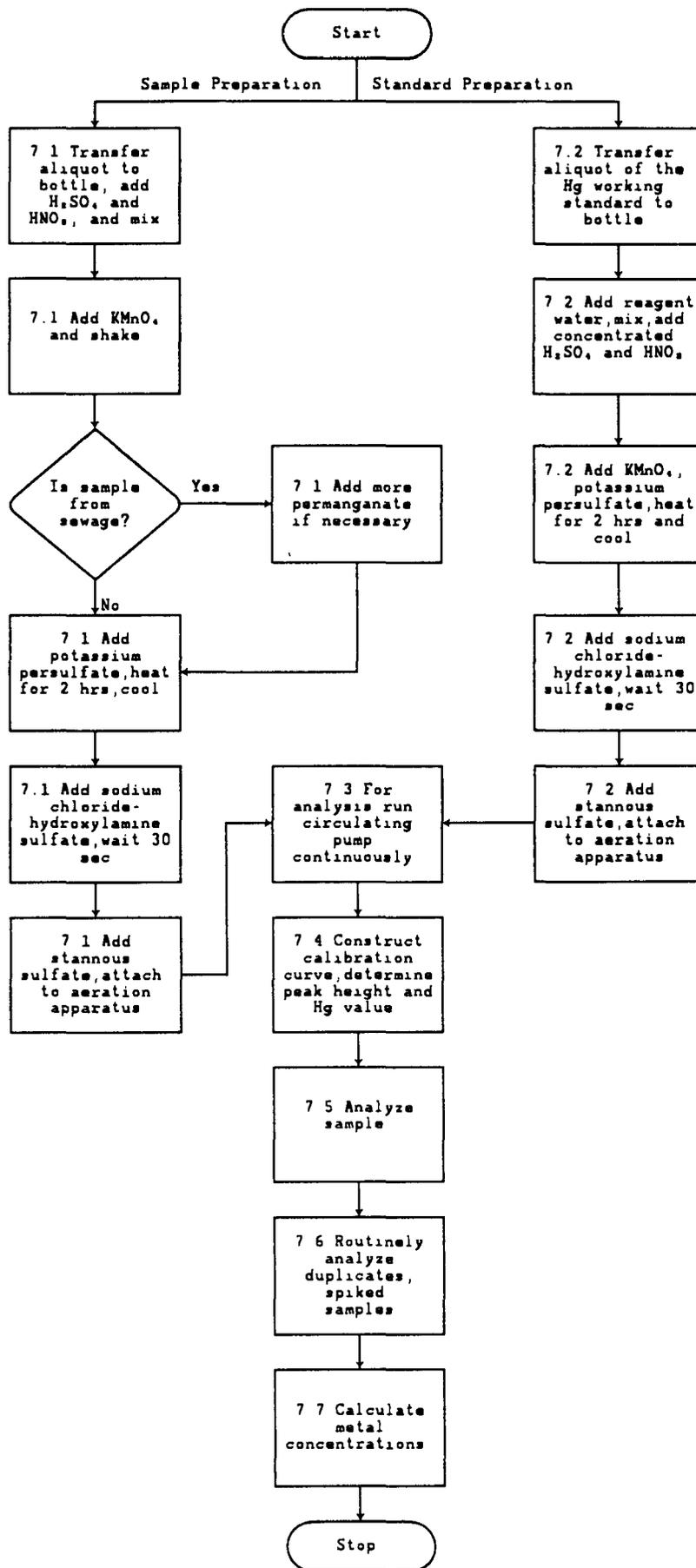
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470A
 MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1.

4.9.1 The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system.

4.9.2 Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M KMnO_4 and 10% H_2SO_4 , or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO₃.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated KMnO_4 solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of KMnO_4 solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

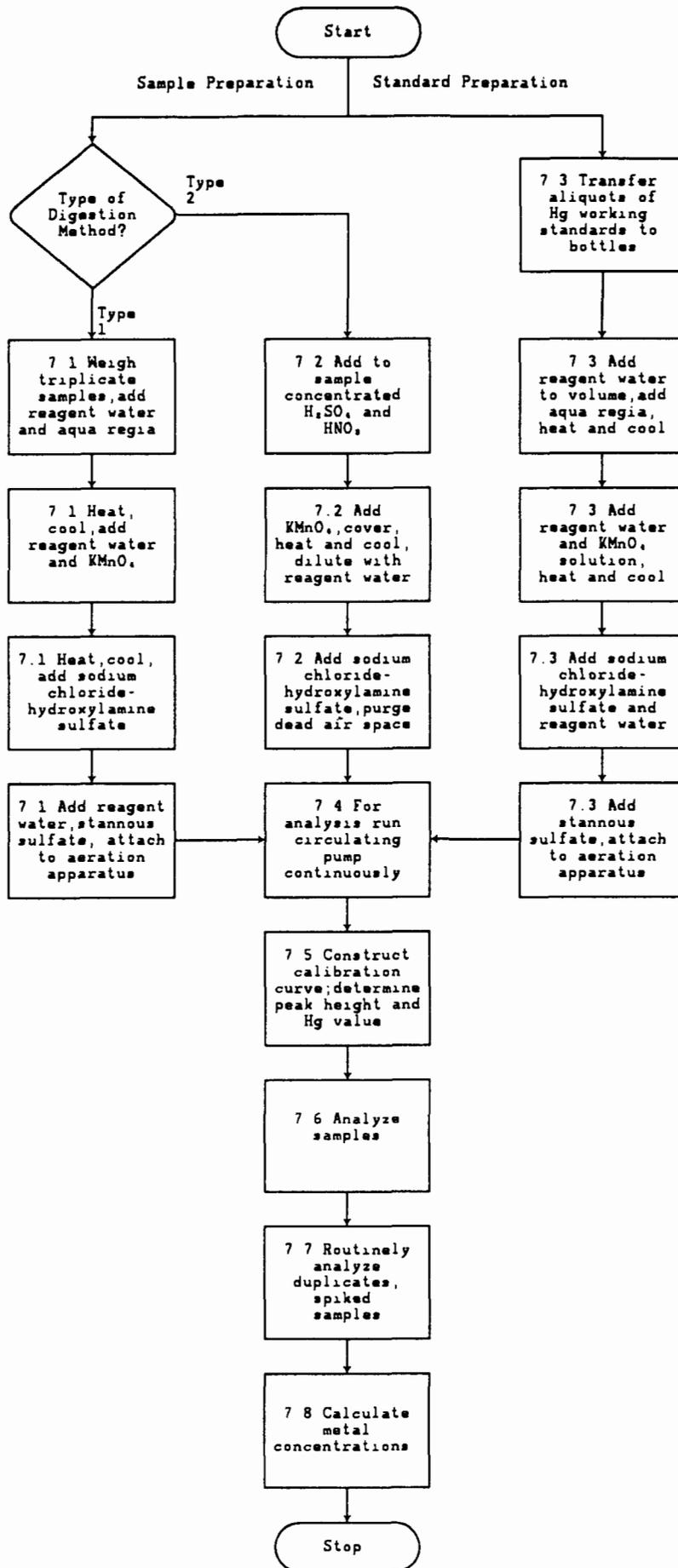
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
 MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7741A

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste. If interferences are present the analyst should consider using Method 7740.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl or sodium borohydrate/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO₃ are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

4.3.1 Medicine dropper: Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 Reaction flask: 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 Gas inlet-outlet tube: Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer: To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube: 10-cm, filled with glass wool to prevent particulate matter from entering the burner.

4.3.6 Flow meter: Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. Reagent water will be interference free. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H₂SO₄ and 400 mL concentrated HCl to 400 mL reagent water and dilute to a final volume of 1 liter with reagent water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL reagent water.

5.7 Stannous chloride solution: Dissolve 100 g SnCl₂ in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H₂SeO₃) in reagent water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of extracts, a 50-mL sample) add 10 mL of concentrated HNO₃ and 12 mL of 18 N H₂SO₄. Evaporate the sample on a hot plate until white SO₃ fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO₃. Maintain an excess of HNO₃ (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 SO₃ fumes, the digestion is complete.

Caution: Venting reaction vessels should be done with caution and only under a fume hood or well ventilated area.

7.1.2 Cool the sample, add about 25 mL reagent water, and again evaporate to SO₃ fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with reagent water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a working stock solution, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 ug Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) 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/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with reagent water containing 1.5 mL HNO_3 /liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with reagent water containing 1.5 mL HNO_3 /liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL 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 sodium borohydrate or 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 or sodium borohydrate into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

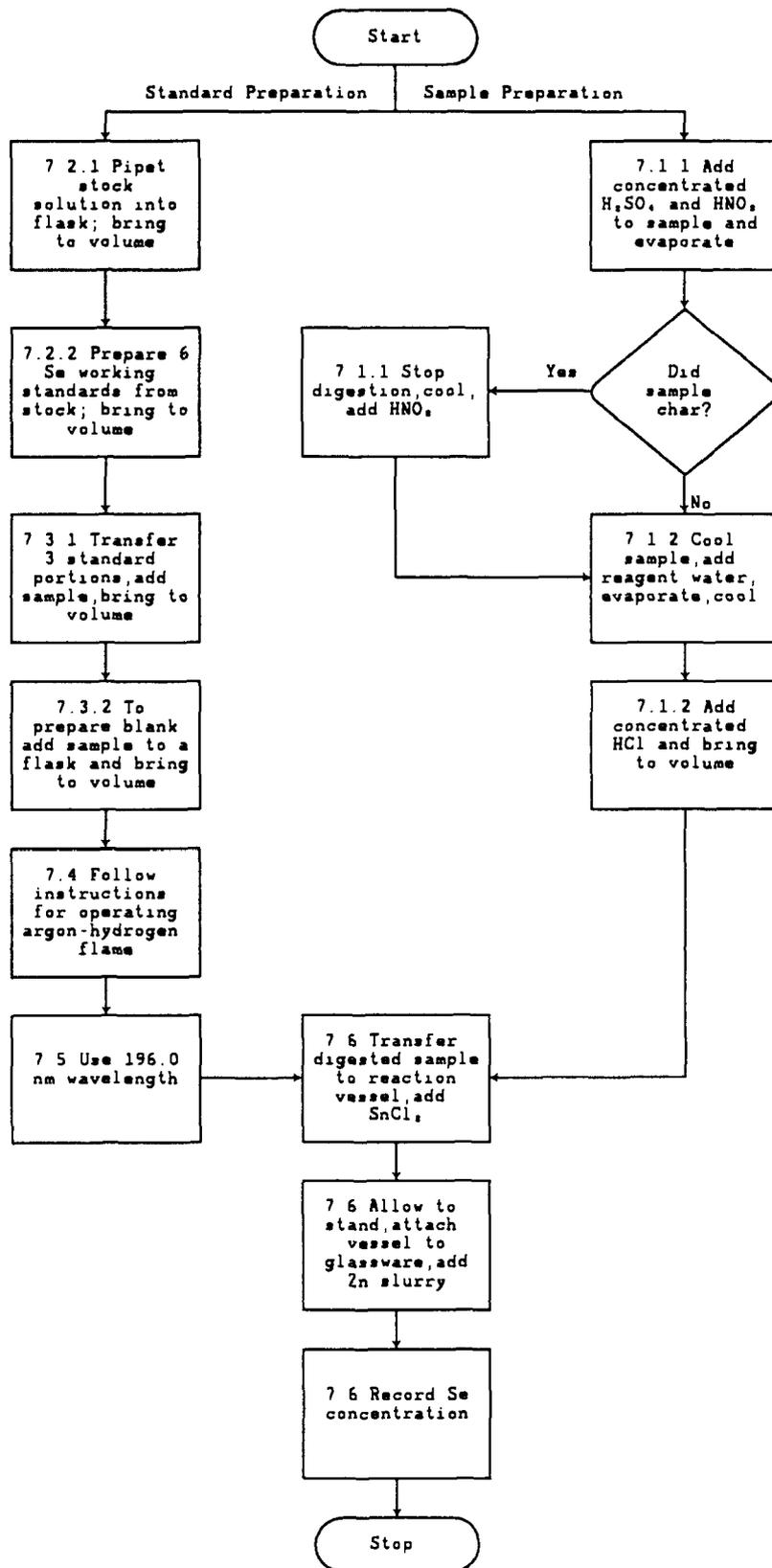
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.

METHOD 7741A
SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7742

SELENIUM (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7742 is an atomic absorption procedure for determining 3 $\mu\text{g/L}$ to 750 $\mu\text{g/L}$ concentrations of selenium in wastes, mobility procedure extracts, soils, and ground water. Method 7742 is approved for sample matrices that contain up to 1000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 10% by weight of the interferents before exceeding 1000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near-dryness at the end of the digestion followed by dilution to volume and degassing the samples upon addition of urea. The selenium is converted to the +4 oxidation state during digestion in HCl. After a 1:10 dilution, selenium is then converted to its volatile hydride using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydride is swept into an air-acetylene flame heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 3 $\mu\text{g/L}$.

3.0 INTERFERENCES

3.1 Very high (>1000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near-dryness followed by reacting each sample with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of teflon and are of compatible sizes to form tight, leak-proof connections (Lachat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting liquid and gaseous products (P. S. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condenser coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17-cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C by an air-acetylene flame.

4.4 Atomic absorption spectrophotometer: Single- or dual- channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Selenium hollow cathode lamp or selenium electrodeless discharge lamp and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water : Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO₃): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H₂O₂): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea (H₂NCONH₂): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

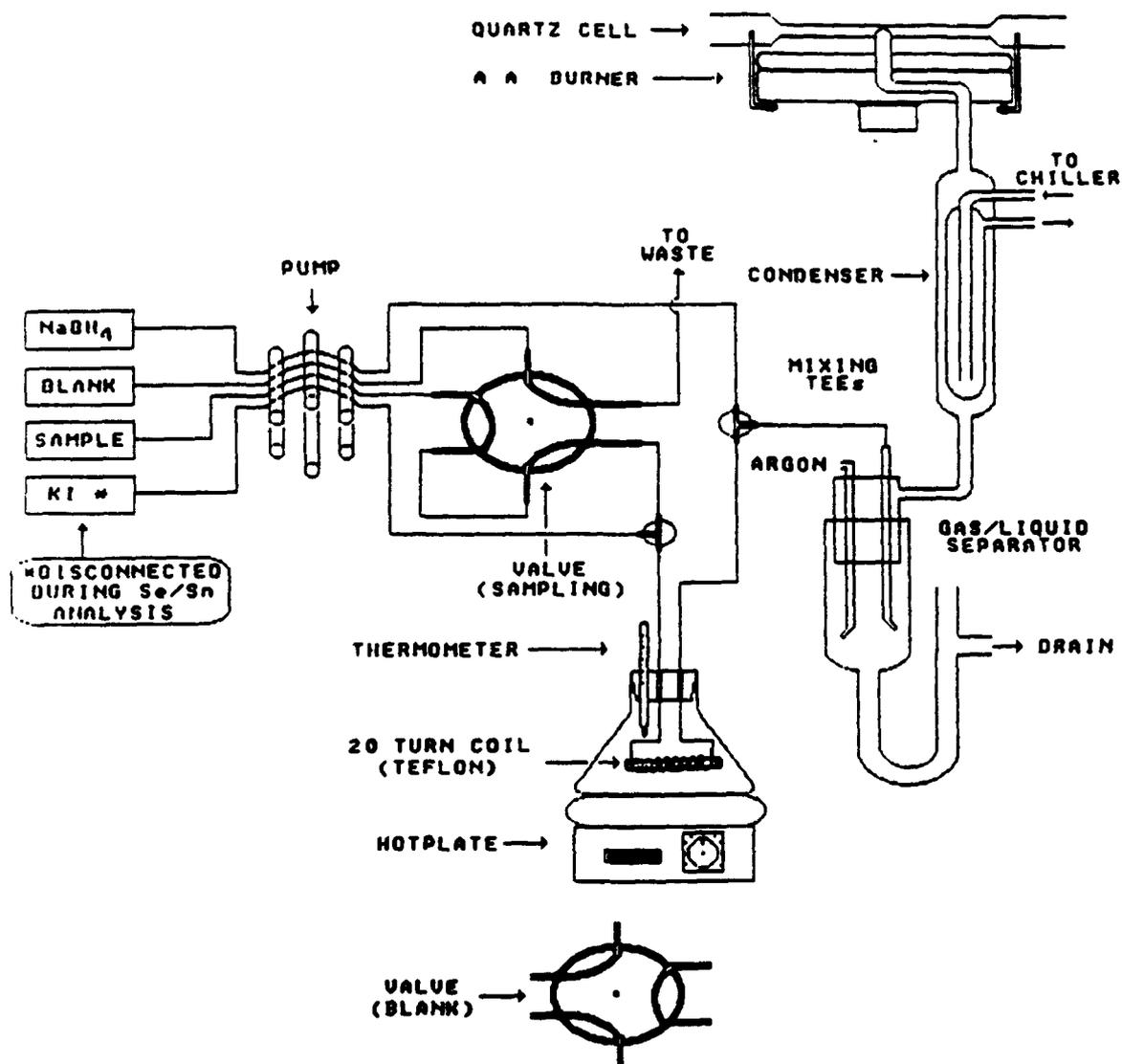


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus setup and an AAS sample introduction system

5.7 4% Sodium Borohydride (NaBH_4): A 4 % sodium borohydride solution (20 g reagent-grade NaBH_4 plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the selenium to its hydride.

5.8 Selenium solutions:

5.8.1 Selenium standard stock solution (1,000 mg/L): Either procure certified aqueous standards from a supplier (Spex, Inorganic Ventures, or equivalent) and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (assay 96.6% of H_2SeO_3) in 200 mL of reagent water (1 mL = 1 mg Se).

5.8.2 Selenium working stock solution: Pipet 1 mL selenium standard stock solution into a 1 L volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3 /liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 μg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

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

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in conversion of selenium to its plus four state; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if the analyte is known to exceed 750 $\mu\text{g}/\text{L}$ or if interferences are expected to exceed 1000 mg/L in the digestate.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data. Close monitoring of each sample is necessary when this critical stage in the digestion is reached.

7.2 Prepare samples for hydride analysis by adding 1.00 g urea, and 20 mL concentrated HCl to a 5.00 mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath to dissolve salts and reduce selenium (at least 30 minutes is suggested). Bring flask to volume with reagent water before analyzing. A ten-fold dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard stock selenium solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 $\mu\text{g Se/L}$.

7.4 If EP extracts (Method 1310) are being analyzed for selenium, the method of standard additions must be used. Spike appropriate amounts of working standard selenium solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, and the borohydride flow around 2.1 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 196.0-nm wavelength and 2.0-nm slit width without background correction. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

CAUTION: The hydride of selenium is very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000.

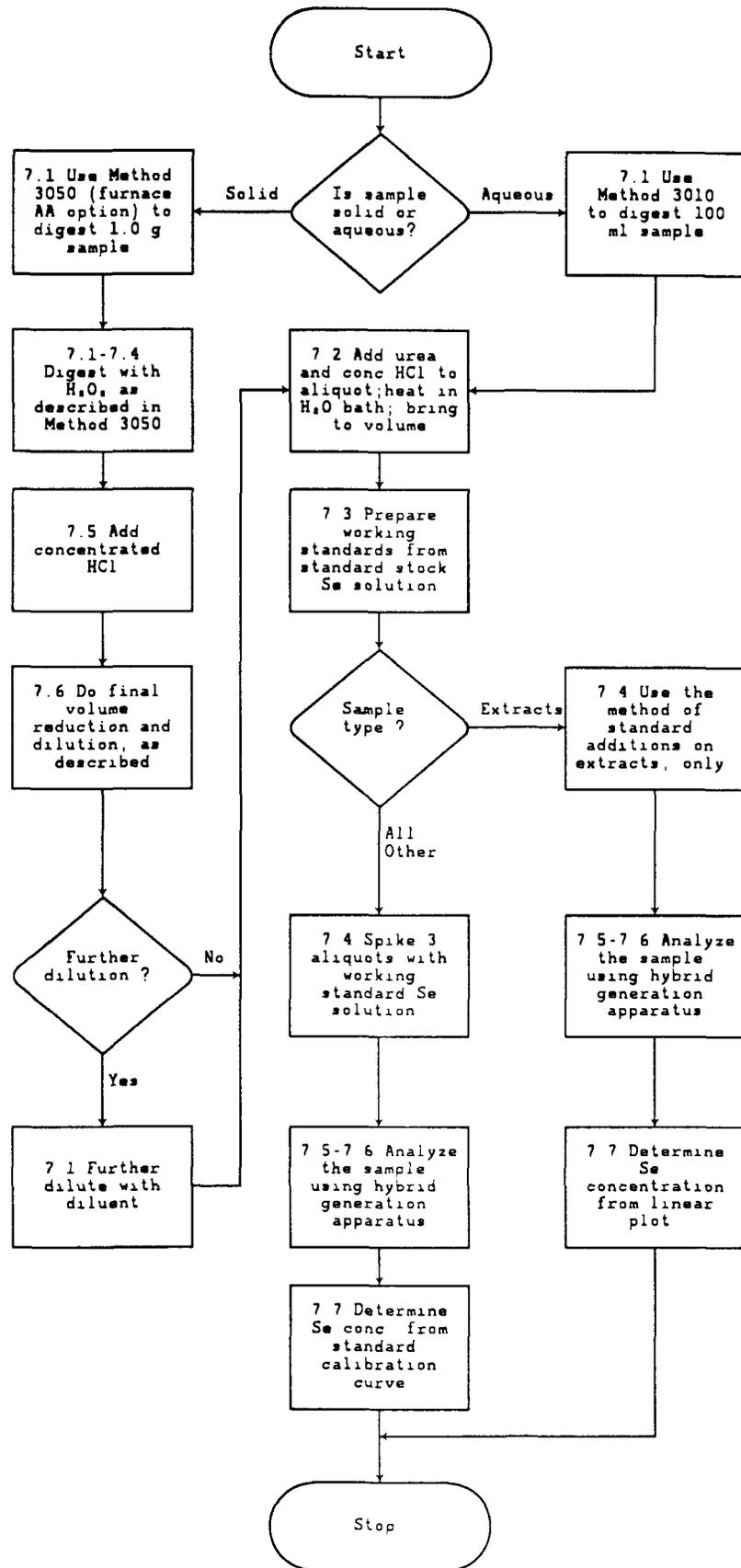
9.0 METHOD PERFORMANCE

9.1 The relative standard deviation obtained by a single laboratory for 7 replicates of a contaminated soil was 18% for selenium at 8.2 ug/L in solution.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.
2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7742
SELENIUM (ATOMIC ABSORPTION, GASEOUS BOROHYDRIDE)



METHOD 7760

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver (CAS Registry Number 7440-22-4) in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Nitric Acid (concentrated), HNO_3 .

5.4 Ammonium Hydroxide (concentrated), NH_4OH .

5.5 Silver Stock Standard Solution (1,000 mg/L), AgNO_3 . Dissolve 0.7874 g anhydrous silver nitrate in water. Add 5 mL HNO_3 and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified aqueous standard from a supplier and verify by comparison with a second standard.

5.6 Silver working standards - These standards should be prepared from silver stock solution to be used as calibration standards at the time of analysis. These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.7 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), in 50 mL of water. Add 12.7 g iodine (I_2) and dilute to 100 mL. Store in a brown bottle.

5.8 Cyanogen iodide solution. Add 4.0 mL ammonium hydroxide, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution to 50 mL of water. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

CAUTION: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.9 Air.

5.10 Acetylene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

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

6.3 Aqueous samples must be acidified to a pH < 2 with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

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

7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated HNO_3 . Cover the beaker with a watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated 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.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a $\text{pH} > 7$ to prevent formation of toxic cyanide under acid conditions. In this case do not adjust the sample volume to the predetermined value until the sample has been neutralized to $\text{pH} > 7$ and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Steps 5.5 and 5.6, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with

ammonium hydroxide. Rinse the pH meter electrodes into the solution with 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 water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1 nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

7.7 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances, or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.8 Analyze all Extraction Procedure (EP) extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.9 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

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

8.2 Calibration curves must be composed of a minimum of a calibration blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

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

8.5 Verify calibration with an independently prepared quality control reference sample every 15 samples.

8.6 Run one spiked replicate sample for every 10 samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Step 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of "Methods for Chemical Analysis of Water and Wastes."

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

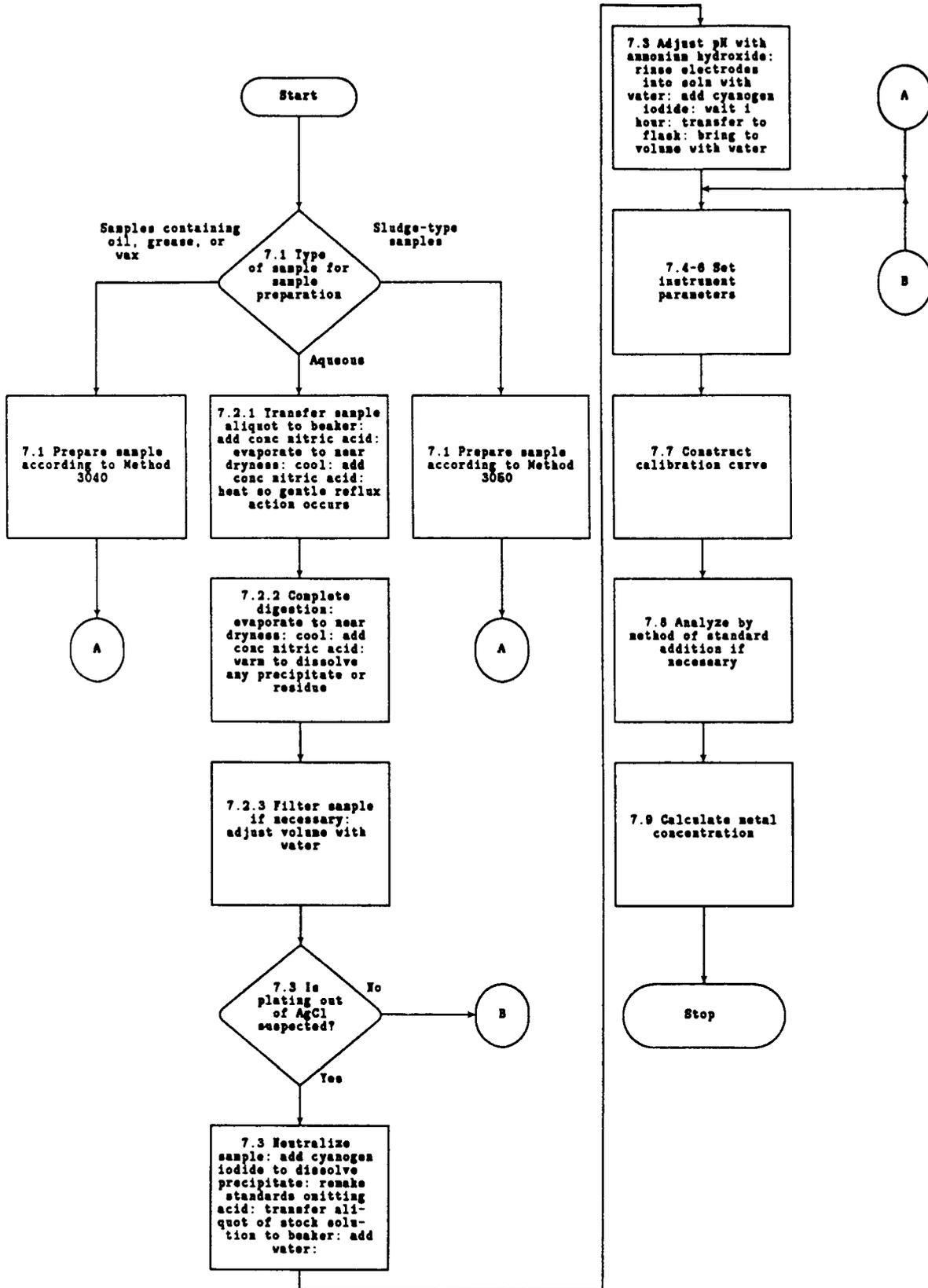
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.
2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, December 1987.
3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 ug/g
Emission control dust	3050	1.8, 4.2 ug/g

METHOD 7760
SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7780

STRONTIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Chemical interference caused by silicon, aluminum, and phosphate are controlled by adding lanthanum chloride. Potassium chloride is added to suppress the ionization of strontium. All samples and standards should contain 1 mL of lanthanum chloride/potassium chloride solution (Step 5.3) per 10 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Strontium hollow cathode lamp.

4.2.2 Wavelength: 460.7 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution: (1.0 mL = 1.0 mg Sr). Dissolve 2.415 g of strontium nitrate, $\text{Sr}(\text{NO}_3)_2$, in 10 mL of concentrated HCl and 700 mL of water. Dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 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 as the samples and cover the range of expected concentrations in the samples. Calibration standards should also contain 1 mL of lanthanum chloride/potassium chloride solution per 10 mL.

5.3 Lanthanum Chloride/Potassium Chloride Solution. Dissolve 11.73 g of lanthanum oxide, La_2O_3 , in a minimum amount of concentrated hydrochloric acid (approximately 50 mL). Add 1.91 g of potassium chloride, KCl. Allow solution to cool to room temperature and dilute to 100 mL with water.

CAUTION: REACTION IS VIOLENT! Add acid slowly and in small portions to control the reaction rate upon mixing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3 - 5 mg/L at a wavelength of 460.7 nm.

Sensitivity: 0.15 mg/L.

Detection limit: 0.03 mg/L.

9.1.1 Recoveries of known amounts of strontium in a series of prepared standards were as given in Table 1.

10.0 REFERENCES

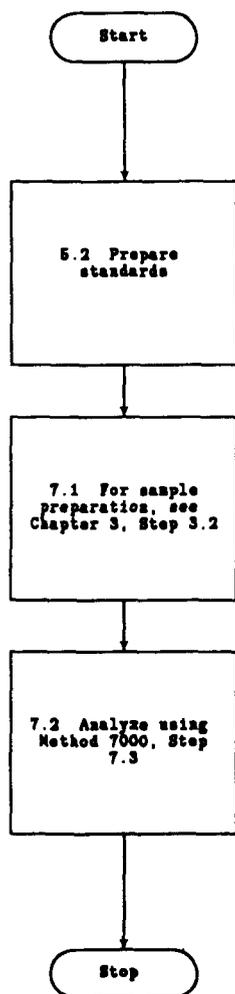
1. Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.

TABLE 1.
RECOVERY

Amount added, mg/L	Amount found, mg/L	Bias	% Bias	Significant (95 % confidence level)
Reagent Water Type II				
1.00	0.998	-0.002	-0.2	no
0.50	0.503	+0.003	+0.6	no
0.10	0.102	+0.002	+2	no
Water of Choice				
1.00	1.03	+0.03	+ 3	no
0.50	0.504	+0.004	+ 0.8	no
0.10	0.086	-0.014	-14	no

Reference: Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.

METHOD 7780
STRONTIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative methods described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly water-soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, at a specified pH (see Table 1), is serially extracted with methylene chloride using a separatory funnel. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method to be used (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel - 2 liter, with Teflon stopcock.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Erlenmeyer flask - 250 mL.

4.9 Syringe - 5 mL.

4.10 Graduated cylinder - 1 liter.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride,

a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H_2SO_4 . Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents

5.6.1 Methylene chloride, CH_2Cl_2 - Pesticide quality or equivalent.

5.6.2 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.6.3 2-Propanol, $CH_3CH(OH)CH_3$ - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C_6H_{12} - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH_3CN - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure 1 liter (nominal) of sample and transfer it quantitatively to the separatory funnel. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Add 1.0 mL of the surrogate standards to all samples, spikes, and blanks (see Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ μ L of each base/neutral analyte and 200 ng/ μ L of each acid analyte in the extract to be analyzed (assuming a 1 μ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Check the pH of the sample with wide-range pH paper and, if necessary, adjust the pH to that indicated in Table 1 for the specific determinative method that will be used to analyze the extract.

7.3 Add 60 mL of methylene chloride to the separatory funnel.

7.4 Seal and shake the separatory funnel vigorously for 1-2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken once. Venting of the

separatory funnel should be into a hood to avoid needless exposure of the analyst to solvent vapors.

7.5 Allow the organic layer to separate from the water phase for a minimum of 10 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 and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the solvent extract in an Erlenmeyer flask. If the emulsion cannot be broken (recovery of < 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in Method 3520, Continuous Liquid-Liquid Extraction.

7.6 Repeat the extraction two more times using fresh portions of solvent (Sections 7.3 through 7.5). Combine the three solvent extracts.

7.7 If further pH adjustment and extraction is required, adjust the pH of the aqueous phase to the desired pH indicated in Table 1. Serially extract three times with 60 mL of methylene chloride, as outlined in Sections 7.3 through 7.5. Collect and combine the extracts and label the combined extract appropriately.

7.8 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral or base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.9 Perform the concentration (if necessary) using the Kuderna-Danish (K-D) Technique (Sections 7.10.1 through 7.10.4).

7.10 K-D Technique

7.10.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the Erlenmeyer flask, which contained the solvent extract, with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.10.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes.

7.10.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.11, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.10.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.11.1) or nitrogen blowdown technique (7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro-Snyder Column Technique

7.11.1.1 If further concentration is indicated in Table 1, add another clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 0.2 mL of extraction solvent. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.11.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 ml, semivolatile analytes may be lost.

7.12 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

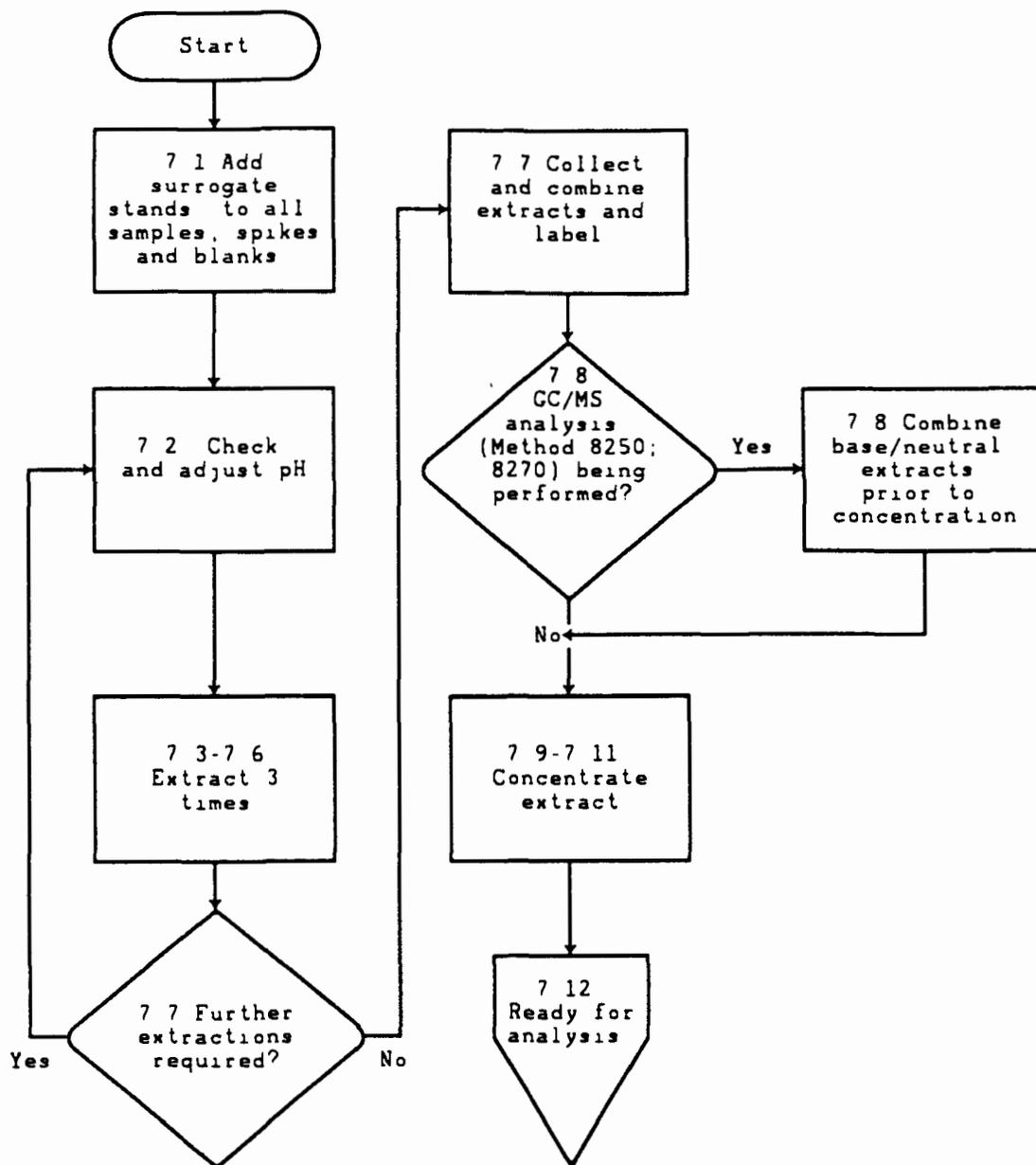
1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0, 10.0 ^a
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250 ^{bc}	>11	<2	none	-	-	1.0
8270 ^{bd}	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

- a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.
- b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.
- c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Section 3.2).
- d Extraction pH sequence may be reversed to better separate acid and neutral waste components. Excessive pH adjustments may result in the loss of some analytes (see Section 3.2).

METHOD 3510B
SEPARATORY FUNNEL LIQUID-LIQUID EXTRACTION



METHOD 3520B

CONTINUOUS LIQUID-LIQUID EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for isolating organic compounds from aqueous samples. The method also describes concentration techniques suitable for preparing the extract for the appropriate determinative steps described in Section 4.3 of Chapter Four.

1.2 This method is applicable to the isolation and concentration of water-insoluble and slightly soluble organics in preparation for a variety of chromatographic procedures.

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

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, usually 1 liter, is placed into a continuous liquid-liquid extractor, adjusted, if necessary, to a specific pH (see Table 1), and extracted with organic solvent for 18-24 hours. The extract is dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative method being employed (see Table 1 for appropriate exchange solvents).

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 Under basic extraction conditions required to separate analytes for the packed columns of Method 8250, the decomposition of some analytes has been demonstrated. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenols may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510. Methods 3520/8270, 3510/8270, and 3510/8250, respectively, are preferred over Method 3520/8250 for the analysis of these classes of compounds.

4.0 APPARATUS AND MATERIALS

4.1 Continuous liquid-liquid extractor - Equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Kontes 584200-0000, 584500-0000, 583250-0000, or equivalent).

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - 2 mL, glass with Teflon lined screw-caps or crimp tops.

4.7 pH indicator paper - pH range including the desired extraction pH.

4.8 Heating mantle - Rheostat controlled.

4.9 Syringe - 5 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Reagents should be stored in glass to prevent the leaching of contaminants from plastic containers.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium hydroxide solution (10N), NaOH. Dissolve 40 g NaOH in organic-free reagent water and dilute to 100 mL.

5.4 Sodium sulfate (granular, anhydrous), Na₂SO₄. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.5 Sulfuric acid solution (1:1 v/v), H₂SO₄. Slowly add 50 mL of H₂SO₄ (sp. gr. 1.84) to 50 mL of organic-free reagent water.

5.6 Extraction/exchange solvents

5.6.1 Methylene chloride, CH₂Cl₂ - Pesticide quality or equivalent.

5.6.2 Hexane, C₆H₁₄ - Pesticide quality or equivalent.

5.6.3 2-Propanol, (CH₃)₂CHOH - Pesticide quality or equivalent.

5.6.4 Cyclohexane, C₆H₁₂ - Pesticide quality or equivalent.

5.6.5 Acetonitrile, CH₃CN - Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Using a 1 liter graduated cylinder, measure out 1 liter (nominal) of sample and transfer it quantitatively to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to the pH indicated in Table 1 using 1:1 (V/V) sulfuric acid or 10 N sodium hydroxide. Pipet 1.0 mL of the surrogate standard spiking solution into each sample into the extractor and mix well. (See Method 3500 and the determinative method to be used, for details on the surrogate standard solution and the matrix spike solution.) For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.2 Add 300-500 mL of methylene chloride to the distilling flask. Add several boiling chips to the flask.

7.3 Add sufficient water to the extractor to ensure proper operation and extract for 18-24 hours.

7.4 Allow to cool; then detach the boiling flask. If extraction at a secondary pH is not required (see Table 1), the extract is dried and concentrated using one of the techniques referred to in Section 7.7.

7.5 Carefully, while stirring, adjust the pH of the aqueous phase to the second pH indicated in Table 1. Attach a clean distilling flask containing 500 mL of methylene chloride to the continuous extractor. Extract for 18-24 hours, allow to cool, and detach the distilling flask.

7.6 If performing GC/MS analysis (Method 8270), the acid/neutral and base extracts may be combined prior to concentration. However, in some situations, separate concentration and analysis of the acid/neutral and base extracts may be preferable (e.g. if for regulatory purposes the presence or absence of specific acid/neutral and base compounds at low concentrations must be determined, separate extract analyses may be warranted).

7.7 Perform concentration (if necessary) using the Kuderna-Danish (K-D) Technique (Sections 7.8.1 through 7.8.4).

7.8 K-D Technique

7.8.1 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20-30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

7.8.2 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

7.8.3 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent, a new boiling chip, and reattach the Snyder column. Concentrate the extract, as described in Section 7.9, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.8.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or

exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques outlined in Section 7.9 or adjusted to 10.0 mL with the solvent last used.

7.9 If further concentration is indicated in Table 1, either the micro-Snyder column technique (7.9.1) or nitrogen blowdown technique (7.9.2) is used to adjust the extract to the final volume required.

7.9.1 Micro-Snyder Column Technique

7.9.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, rinse the flask and its lower joints into the concentrator tube with 0.2 mL of methylene chloride or exchange solvent, and adjust the final volume to 1.0 to 2.0 mL, as indicated in Table 1, with solvent.

7.9.2 Nitrogen Blowdown Technique

7.9.2.1 Place the concentrator tube in a warm bath (35°C) and evaporate the solvent volume to 0.5 mL using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: New plastic tubing must not be used between the carbon trap and the sample, since it may introduce interferences.

7.9.2.2 The internal wall of the tube must be rinsed down several times with methylene chloride or appropriate solvent during the operation. During evaporation, the tube solvent level must be positioned to avoid water condensation. Under normal procedures, the extract must not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatiles may be lost.

7.10 The extract may now be analyzed for the target analytes using the appropriate determinative technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days it should be transferred to a vial with a Teflon lined screw-cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks, matrix spike, or replicate samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample-preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

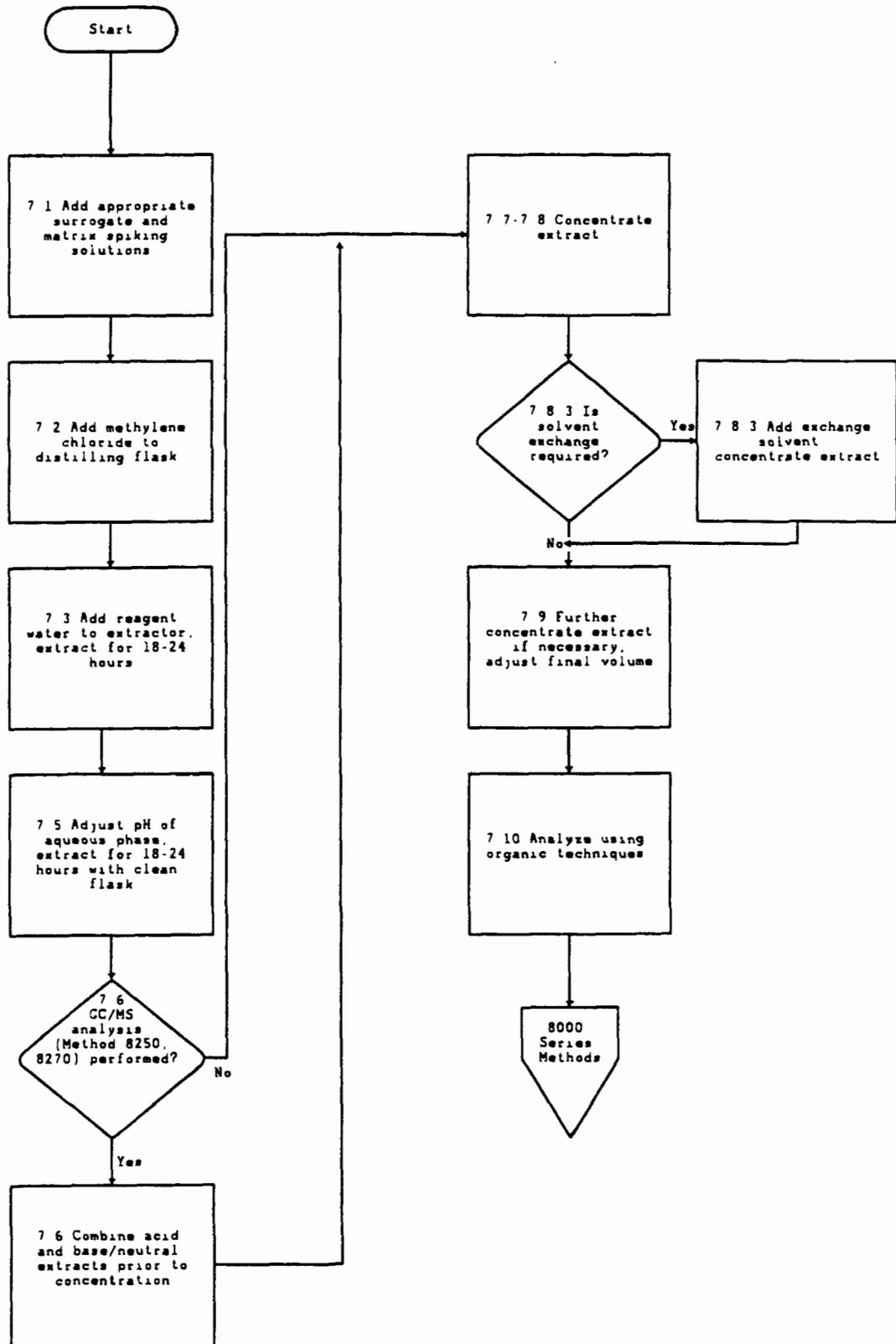
1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

Determinative method	Initial extraction pH	Secondary extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040	≤2	none	2-propanol	hexane	1.0	1.0, 10.0 ^a
8060	as received	none	hexane	hexane	2.0	10.0
8061	as received	none	hexane	hexane	2.0	10.0
8070	as received	none	methanol	methylene chloride	2.0	10.0
8080	5-9	none	hexane	hexane	10.0	10.0
8081	5-9	none	hexane	hexane	10.0	10.0
8090	5-9	none	hexane	hexane	2.0	1.0
8100	as received	none	none	cyclohexane	2.0	1.0
8110	as received	none	hexane	hexane	2.0	10.0
8120	as received	none	hexane	hexane	2.0	1.0
8121	as received	none	hexane	hexane	2.0	1.0
8140	6-8	none	hexane	hexane	10.0	10.0
8141	as received	none	hexane	hexane	10.0	10.0
8250 ^{b,c}	>11	<2	none	-	-	1.0
8270 ^{b,d}	<2	>11	none	-	-	1.0
8310	as received	none	acetonitrile	-	-	1.0
8321	as received	none	methanol	-	-	1.0
8410	as received	none	methylene chloride	methylene chloride	10.0	0.0 (dry)

- a Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optional derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.
- b The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.
- c Loss of phthalate esters, organochlorine pesticides and phenols can occur under these extraction conditions (see Section 3.2).
- d If further separation of major acid and neutral components is required, Method 3650, Acid-Base Partition Cleanup, is recommended. Reversal of the Method 8270 pH sequence is not recommended as analyte losses are more severe under the base first continuous extraction (see Section 3.2).

METHOD 3520B
CONTINUOUS LIQUID-LIQUID EXTRACTION



METHOD 3540B

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 This method is applicable to the isolation and concentration of water insoluble and slightly water soluble organics in preparation for a variety of chromatographic procedures.

2.0 SUMMARY OF METHOD

2.1 The solid sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is then dried, concentrated (if necessary), and, as necessary, exchanged into a solvent compatible with the cleanup or determinative step being employed.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Soxhlet extractor - 40 mm ID, with 500 mL round bottom flask.

4.2 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.3 Kuderna-Danish (K-D) apparatus

4.3.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.5 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.6 Vials - Glass, 2 mL capacity, with Teflon lined screw or crimp top.

4.7 Glass or paper thimble or glass wool - Contaminant free.

4.8 Heating mantle - Rheostat controlled.

4.9 Disposable glass pasteur pipet and bulb.

4.10 Apparatus for determining percent dry weight.

4.10.1 Oven - Drying.

4.10.2 Desiccator.

4.10.3 Crucibles - Porcelain or disposable aluminum.

4.11 Apparatus for grinding

4.12 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents

5.4.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems:

5.4.1.1 Acetone/Hexane (1:1) (v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$. Pesticide quality or equivalent.

NOTE: This solvent system has lower disposal cost and lower toxicity.

5.4.1.2 Methylene chloride/Acetone (1:1 v/v), $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COCH}_3$. Pesticide quality or equivalent.

5.4.2 Other samples shall be extracted using the following:

5.4.2.1 Methylene chloride, CH_2Cl_2 . Pesticide quality or equivalent.

5.4.2.2 Toluene/Methanol (10:1) (v/v), $\text{C}_6\text{H}_5\text{CH}_3/\text{CH}_3\text{OH}$. Pesticide quality or equivalent.

5.5 Exchange solvents

5.5.1 Hexane, C_6H_{14} . Pesticide quality or equivalent.

5.5.2 2-Propanol, $(\text{CH}_3)_2\text{CHOH}$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12} . Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN . Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analysis, Section 4.1.

7.0 PROCEDURE

7.1 Sample Handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can

be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 10 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling these difficult matrixes.

7.2 Determination of sample % dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be overdried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay overdrying of the weighed-out portion until other analytical results are available.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Blend 10 g of the solid sample with 10 g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 1.0 mL of the surrogate standard spiking solution onto the sample (see Method 3500 for details on the surrogate standard and matrix spiking solutions). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/μL of each base/neutral analyte and 200 ng/μL of each acid analyte in the extract to be analyzed (assuming a 1 μL injection). If Method 3640, Gel Permeation Chromatography Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.4 Place approximately 300 mL of the extraction solvent (Section 5.4) into a 500 mL round bottom flask containing one or two clean boiling chips. Attach the flask to the extractor and extract the sample for 16-24 hours at 4-6 cycles/hr.

7.5 Allow the extract to cool after the extraction is complete.

7.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporation flask.

7.7 Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Wash the extractor flask and sodium sulfate column with 100 to 125 mL of extraction solvent to complete the quantitative transfer.

7.8 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes.

7.9 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add approximately 50 mL of the exchange solvent and a new boiling chip, and reattach the Snyder column. Concentrate the extract as described in Section 7.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.10 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the techniques described in Section 7.11 or adjusted to 10.0 mL with the solvent last used.

7.11 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.11.1) or nitrogen blowdown technique (Section 7.11.2) is used to adjust the extract to the final volume required.

7.11.1 Micro Snyder Column Technique

7.11.1.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of methylene chloride or exchange solvent to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of solvent and add to the

concentrator tube. Adjust the final volume to 1.0-2.0 mL, as indicated in Table 1, with solvent.

7.11.2 Nitrogen Blowdown Technique

7.11.2.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.11.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.12 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 1.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

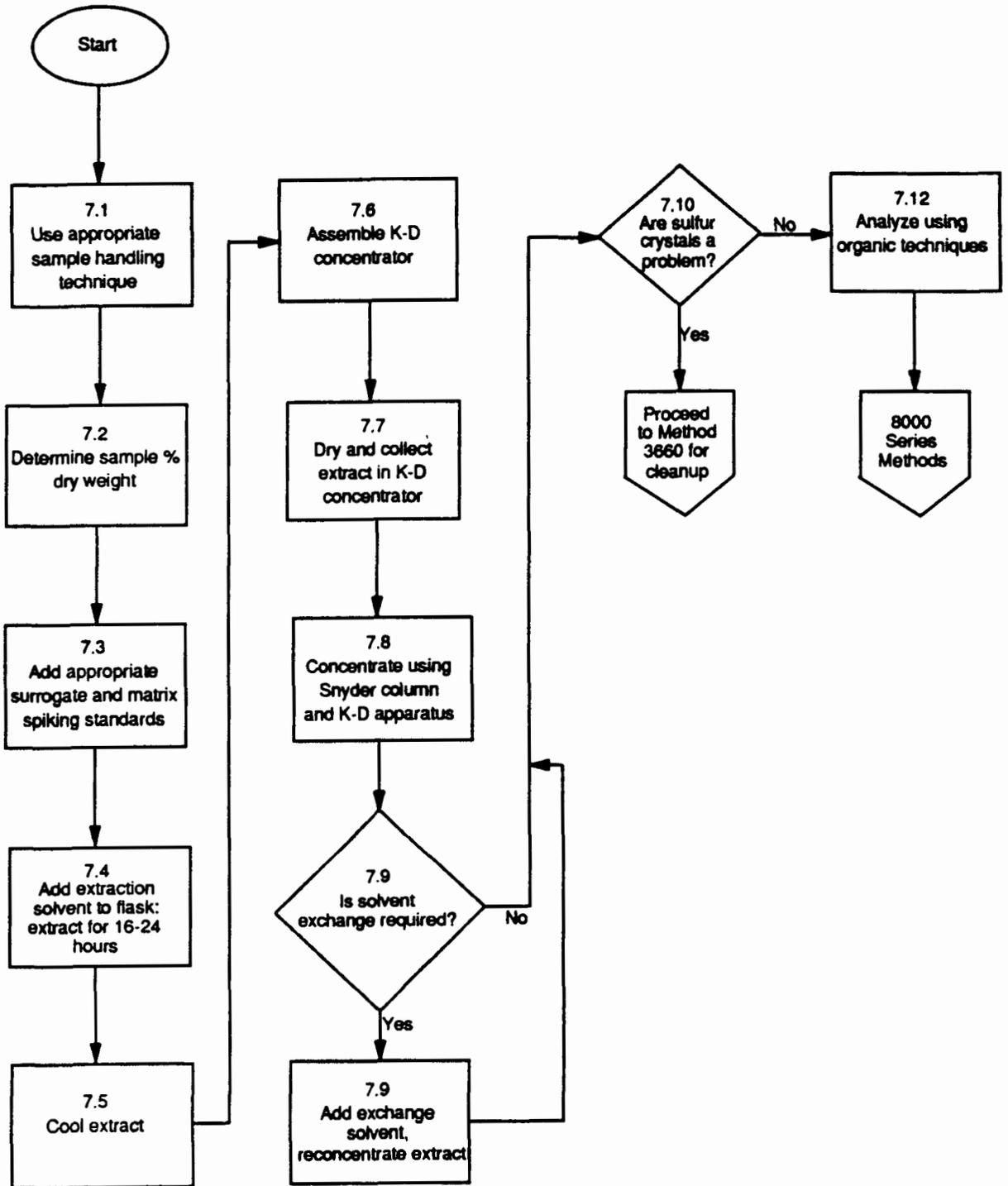
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 ^a	as received	2-propanol	hexane	1.0	1.0, 10.0 ^b
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250 ^{a,c}	as received	none	--	--	1.0
8270 ^c	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

^a To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

^b Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3540B
SOXHLET EXTRACTION



METHOD 3541

AUTOMATED SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3541 describes the extraction of organic analytes from soil, sediment, sludges, and waste solids. The method uses a commercially available, unique, three stage extraction system to achieve analyte recovery comparable to Method 3540, but in a much shorter time. There are two differences between this extraction method and Method 3540. In the initial extraction stage of Method 3541, the sample-loaded extraction thimble is immersed into the boiling solvent. This ensures very rapid intimate contact between the specimen and solvent and rapid extraction of the organic analytes. In the second stage the thimble is elevated above the solvent, and is rinse-extracted as in Method 3540. In the third stage, the solvent is evaporated, as would occur in the Kuderna-Danish (K-D) concentration step in Method 3540. The concentrated extract is then ready for cleanup (Method 3600) followed by measurement of the organic analytes.

1.2 The method is applicable to the extraction and concentration of water insoluble or slightly water soluble polychlorinated biphenyls (PCBs) in preparation for gas chromatographic determination using either Method 8080 or 8081. This method is applicable to soils, clays, solid wastes and sediments containing from 1 to 50 μg of PCBs (measured as Arochlors) per gram of sample. It has been statistically evaluated at 5 and 50 $\mu\text{g}/\text{g}$ of Arochlors 1254 and 1260, and found to be equivalent to Method 3540 (Soxhlet Extraction). Higher concentrations of PCBs are measured following volumetric dilution with hexane.

1.3 The method is also applicable the extraction and concentration of organochlorine pesticides and semivolatile organics in preparation for GC/MS analysis by Method 8270 or by analysis using specific GC or HPLC methods.

2.0 SUMMARY OF METHOD

2.1 Organochlorine pesticides and semivolatile organics: A 10-g solid sample (the sample is pre-mixed with anhydrous sodium sulfate for certain matrices) is placed in an extraction thimble and usually extracted with 50 mL of 1:1 (v/v) acetone/hexane for 60 minutes in the boiling extraction solvent. The thimble with sample is then raised into the rinse position and extracted for an additional 60 minutes. Following the extraction steps, the extraction solvent is concentrated to 1 to 2 mL.

2.2 PCBs: Moist solid samples (e.g., soil/sediment samples) may be air-dried and ground prior to extraction or chemically dried with anhydrous sodium sulfate. The prepared sample is extracted using 1:1 (v/v) acetone:hexane in the automated Soxhlet following the same procedure as outlined for semivolatile organics in Section 2.1. The extract is then concentrated and exchanged into pure hexane prior to final gas chromatographic PCB measurement.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

3.2 The extraction thimble and the o-rings used to seal the extraction cup are both a source of interference. Both should be checked by including a method blank and following the extraction procedure as written. Solvent rinsing or extraction, prior to use, may be necessary to eliminate or reduce interferences. Viton seals contributed least to the interference problem, however, even they contributed some interference peaks when the extraction solvent was analyzed by the electron capture detector. Use of butyl or EPDM rings are not recommended since they were found to contribute significant background when the extraction solvent was 1:1 v/v hexane/acetone or 1:1 v/v methylene chloride/acetone.

4.0 APPARATUS AND MATERIALS

4.1 Automated Soxhlet Extraction System - with temperature-controlled oil bath (Soxtec, or equivalent). Tecator bath oil (catalog number 1000-1886) should be used with the Soxtec. Silicone oil must not be used because it destroys the rubber parts. See Figure 1. The apparatus is used in a hood.

4.2 Accessories and consumables for the automated Soxhlet system. (The catalog numbers are Fisher Scientific based on the use of the Soxtec HT-6, however, other sources that are equivalent are acceptable.)

4.2.1 Cellulose extraction thimbles - 26 mm ID x 60 mm contamination free, catalog number 1522-0034, or equivalent.

4.2.2 Glass extraction cups (80 mL) - (set of six required for the HT-6), catalog number 1000-1820.

4.2.3 Thimble adapters - (set of six required for the HT-6), catalog number 1000-1466.

4.2.4 Viton seals - catalog number 1000-2516.

4.3 Syringes - 100 and 1000 μ L and 5 mL.

4.4 Apparatus for Determining Percent Dry Weight

4.4.1 Drying Oven.

4.4.2 Desiccator.

4.4.3 Crucibles, porcelain.

4.4.4 Balance, analytical.

4.5 Apparatus for grinding - Fisher Cyclotec, Fisher Scientific catalog number 1093, or equivalent.

4.6 Spatula

4.7 Graduated cylinder - 100 mL.

4.8 Aluminum weighing dish - VWR Scientific catalog number 25433-008 or equivalent.

4.9 Graduated, conical-bottom glass tubes - 15 mL, Kimble catalog number 45166 or equivalent, or 10 mL KD concentrator tube.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents:

5.4.1 Organochlorine pesticides/PCB extraction:

5.4.1.1 Acetone/hexane (1:1 v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$.
Pesticide quality or equivalent.

5.4.2 Semivolatile organics extraction:

5.4.2.1 Acetone/hexane (1:1 v/v), $\text{CH}_3\text{COCH}_3/\text{C}_6\text{H}_{14}$.
Pesticide quality or equivalent.

5.4.2.2 Acetone/methylene chloride (1:1 v/v),
 $\text{CH}_3\text{COCH}_3/\text{CH}_2\text{Cl}_2$. Pesticide quality or equivalent.

5.5 Hexane, C_6H_{14} . Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.1 PCBs or high-boiling organochlorine pesticides - Air-dry the sample at room temperature for 48 hours in a glass tray or on hexane-cleaned aluminum foil, or dry the sample by mixing with anhydrous sodium sulfate until a free-flowing powder is obtained (see Section 7.2).

NOTE: Dry, finely ground soil/sediment allows the best extraction efficiency for non-volatile, non-polar organics, e.g., PCBs, 4,4'-DDT, etc. Air-drying is not appropriate for the analysis of the more volatile organochlorine pesticides (e.g. the BHCs) or the more volatile of the semivolatile organics because of losses during the drying process.

7.1.2 Dried sediment/soil and dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinding apparatus to yield at least 20 g after grinding. Disassemble grinder between samples, according to manufacturer's instructions, and clean with soap and water, followed by acetone and hexane rinses.

NOTE: The same warning on loss of volatile analytes applies to the grinding process. Grinding should only be performed when analyzing for non-volatile organics.

7.1.3 Gummy, fibrous, or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. If grinding of these materials is preferred, the addition and mixing of anhydrous sodium sulfate with the sample (1:1) may improve grinding efficiency. The professional judgment of the analyst is required for handling such difficult matrices.

7.1.4 Multiple phase waste samples - Samples consisting of multiple phases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.2 For sediment/soil (especially gummy clay) that is moist and cannot be air-dried because of loss of volatile analytes - Mix 5 g of sample with 5 g of anhydrous sodium sulfate in a small beaker using a spatula. Use this approach for any solid sample that requires dispersion of the sample particles to ensure greater solvent contact throughout the sample mass.

7.3 Determination of sample percent dry weight - In certain cases, sample results are desired based on dry weight basis. When such data are desired, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from the drying of a heavily contaminated hazardous waste sample.

7.3.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.4 Check the heating oil level in the automated Soxhlet unit and add oil if needed. See service manual for details. Set the temperature on the service unit at 140°C when using hexane-acetone (1:1, v/v) as the extraction solvent.

7.5 Press the "MAINS" button; observe that the switch lamp is now "ON".

7.6 Open the cold water tap for the reflux condensers. Adjust the flow to 2 L/min to prevent solvent loss through the condensers.

7.7 Weigh 10 g of sample into extraction thimbles. For samples mixed with anhydrous sodium sulfate, transfer the entire contents of the beaker (Section 7.2) to the thimble. Add surrogate spikes to each sample and the matrix spike/matrix spike duplicate to the selected sample.

NOTE: When surrogate spikes and/or matrix spikes contain relatively volatile compounds (e.g., trichlorobenzenes, BHCs, etc.), steps 7.8, 7.9, and 7.10 must be performed quickly to avoid evaporation losses of these compounds. As the spike is added to the sample in each thimble, the thimble should immediately be transferred to the condenser and lowered into the extraction solvent.

7.8 Immediately transfer the thimbles containing the weighed samples into the condensers. Raise the knob to the "BOILING" position. The magnet will now fasten to the thimble. Lower the knob to the "RINSING" position. The thimble will now hang just below the condenser valve.

7.9 Insert the extraction cups containing boiling chips, and load each with 50 mL of extraction solvent (normally 1:1 (v/v) hexane:acetone, see Section 5.4). Using the cup holder, lower the locking handle, ensuring that the safety catch engages. The cups are now clamped into position. (The seals must be pre-rinsed or pre-extracted with extraction solvent prior to initial use.)

7.10 Move the extraction knobs to the "BOILING" position. The thimbles are now immersed in solvent. Set the timer for 60 minutes. The condenser valves must be in the "OPEN" position. Extract for the preset time.

7.11 Move the extraction knobs to the "RINSING" position. The thimbles will now hang above the solvent surface. Set timer for 60 minutes. Condenser valves are still open. Extract for the preset time.

7.12 After rinse time has elapsed, close the condenser valves by turning each a quarter-turn, clockwise.

7.13 When all but 2 to 5 mL of solvent have been collected, open the system and remove the cups.

7.14 Transfer the contents of the cups to 15 mL graduated, conical-bottom glass tubes. Rinse the cups using hexane (methylene chloride if 1:1 methylene chloride-acetone was used for extraction and analysis is by GC/MS) and add the rinsates to the glass tubes. Concentrate the extracts to 1 to 10 mL. The final volume is dependent on the determinative method and the quantitation limit required. Transfer a portion to a GC vial and store at 4°C until analyses are performed.

NOTE: The recovery solvent volume can be adjusted by adding solvent at the top of the condensers. For more details concerning use of the extractor, see the operating manual for the automated extraction system.

7.15 Shutdown

7.15.1 Turn "OFF" main switch.

7.15.2 Turn "OFF" cold water tap.

7.15.3 Ensure that all condensers are free of solvent. Empty the solvent that is recovered in the evaporation step into an appropriate storage container.

7.16 The extract is now ready for cleanup or analysis, depending on the extent of interfering co-extractives. See Method 3600 for guidance on cleanup methods and Method 8000 for guidance on determinative methods. Certain cleanup and/or determinative methods may require a solvent exchange prior to cleanup and/or determination.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for general quality control procedures and to Method 3500 for specific extraction and sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free solid matrix (e.g., reagent sand) method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted, or when 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. This is especially important because of the possibility of interferences being extracted from the extraction cup seal.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, and a laboratory control sample, unless the determinative method provides other guidance. Also, routinely check the integrity of the instrument seals.

8.4 Surrogate standards must be added to all samples when specified in the appropriate determinative method.

9.0 METHOD PERFORMANCE

9.1 Multi-laboratory accuracy and precision data were obtained for PCBs in soil. Eight laboratories spiked Arochlors 1254 and 1260 into three portions of 10 g of Fuller's Earth on three non-consecutive days followed by immediate extraction using Method 3541. Six of the laboratories spiked each Arochlor at 5 and 50 mg/kg and two laboratories spiked each Arochlor at 50 and 500 mg/kg. All extracts were analyzed by Oak Ridge National Laboratory, Oak Ridge, TN, using Method 8080. These data are listed in a table found in Methods 8080 and 8081, and were taken from Reference 1.

9.2 Single-laboratory accuracy data were obtained for chlorinated hydrocarbons, nitroaromatics, haloethers, and organochlorine pesticides in a clay soil. The spiking concentrations ranged from 500 to 5000 $\mu\text{g}/\text{kg}$, depending on the sensitivity of the analyte to the electron capture detector. The spiking solution was mixed into the soil during addition and then immediately transferred to the extraction device and immersed in the extraction solvent. The data represents a single determination. Analysis was by capillary column gas chromatography/electron capture detector following Methods 8081 for the organochlorine pesticides, 8091 for the nitroaromatics, 8111 for the hydrocarbons, and 8121 for the chlorinated hydrocarbons. These data are listed in a table located in their respective methods and were taken from Reference 2.

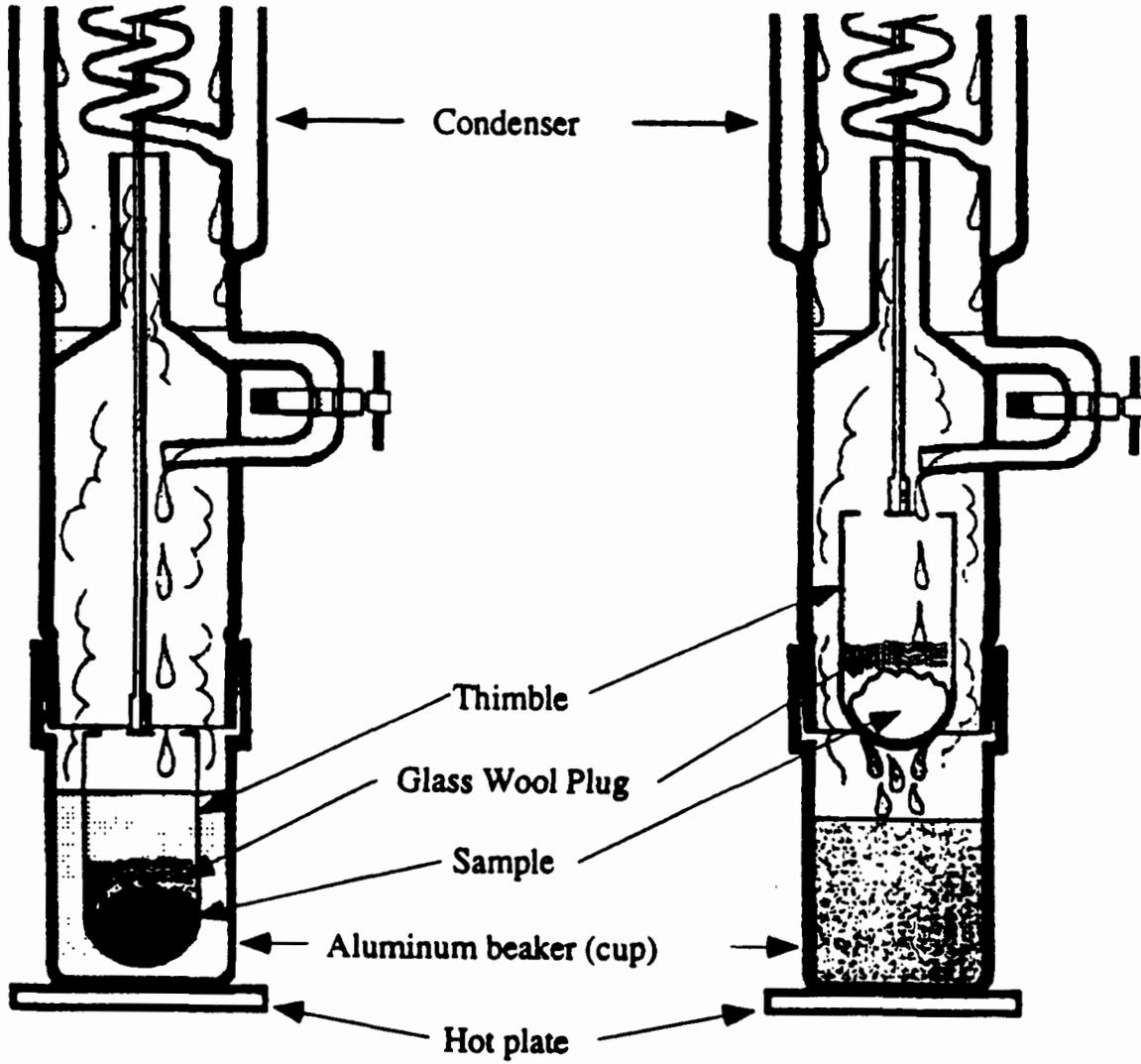
9.3 Single-laboratory accuracy and precision data were obtained for semivolatile organics in soil by spiking at a concentration of 6 mg/kg for each compound. The spiking solution was mixed into the soil during addition and then allowed to equilibrate for approximately 1 hr prior to extraction. Three determinations were performed and each extract was analyzed by gas chromatography/mass spectrometry following Method 8270. The low recovery of the more volatile compounds is probably due to volatilization losses during equilibration. These data are listed in a Table located in Method 8270 and were taken from Reference 2.

10.0 REFERENCES

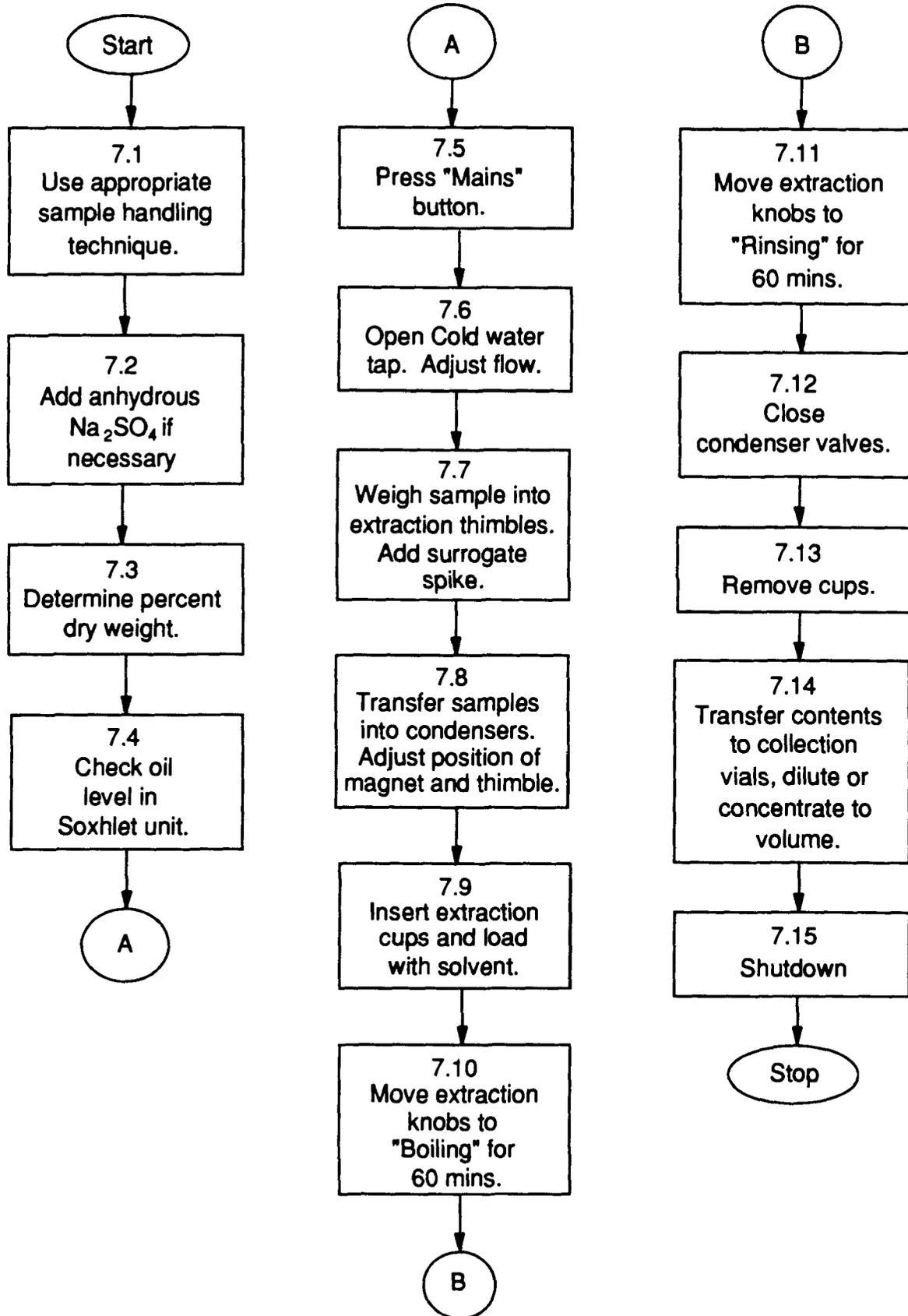
1. Stewart, J. "Intra-Laboratory Recovery Data for the PCB Extraction Procedure"; Oak Ridge National Laboratory, Oak Ridge, TN, 37831-6138; October 1989.

2. Lopez-Avila, V. (Beckert, W., Project Officer), "Development of a Soxtec Extraction Procedure for Extracting Organic Compounds from Soils and Sediments", EPA 600/X-91/140, US EPA, Environmental Monitoring Systems Laboratory-Las Vegas, October 1991.

Figure 1
Automated Soxhlet Extraction System



METHOD 3541
AUTOMATED SOXHLET EXTRACTION



METHOD 3550A

ULTRASONIC EXTRACTION

See DISCLAIMER-1. See manufacturer's specifications for operational settings.

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semi-volatile organic compounds from solids such as soils, sludges, and wastes. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

1.2 The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (individual organic components of ≤ 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of > 20 mg/kg) is much simpler and therefore faster.

1.3 It is highly recommended that the extracts be cleaned up prior to analysis. See Chapter Four (Cleanup), Section 4.2.2, for applicable methods.

2.0 SUMMARY OF METHOD

2.1 Low concentration method - A 30 g sample is mixed with anhydrous sodium sulfate to form a free flowing powder. This is solvent extracted three times using ultrasonic extraction. A portion of the extract is removed for cleanup and/or analysis.

2.2 Medium/high concentration method - A 2 g sample is mixed with anhydrous sodium sulfate. This mixture is solvent extracted three times using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding dry waste samples.

4.2 Ultrasonic preparation - A horn type device equipped with a titanium tip, or a device that will give equivalent performance, shall be used.

4.2.1 Ultrasonic Disrupter - The disrupter must have a minimum power wattage of 300 watts, with pulsing capability. A device designed to reduce the cavitation sound is recommended. Follow the manufacturers instructions for preparing the disrupter for extraction of samples with low and medium/high concentration.

Use a 3/4" horn for the low concentration method and a 1/8" taperec microtip attached to a 1/2" horn for the medium/high concentration method.

4.3 Sonabox - Recommended with above disrupters for decreasing cavitation sound (Heat Systems - Ultrasonics, Inc., Model 432B or equivalent).

4.4 Apparatus for determining percent dry weight.

4.4.1 Oven - Drying.

4.4.2 Desiccator.

4.4.3 Crucibles - Porcelain or disposable aluminum.

4.5 Pasteur glass pipets - 1 mL, disposable.

4.6 Beakers - 400 mL.

4.7 Vacuum or pressure filtration apparatus.

4.7.1 Buchner funnel.

4.7.2 Filter paper - Whatman No. 41 or equivalent.

4.8 Kuderna-Danish (K-D) apparatus.

4.8.1 Concentrator tube - 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.8.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.8.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.8.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.9 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.11 Balance - Top loading, capable of accurately weighing to the nearest 0.01 g.

4.12 Vials - 2 mL, for GC autosampler, with Teflon lined screw caps or crimp tops.

4.13 Glass scintillation vials - 20 mL, with Teflon lined screw caps.

4.14 Spatula - Stainless steel or Teflon.

4.15 Drying column - 20 mm ID Pyrex chromatographic column with Pyrex glass wool at bottom.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.16 Syringe - 5 mL.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise specified, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400 °C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Extraction solvents.

5.4.1 Low concentration soil/sediment and aqueous sludge samples shall be extracted using a solvent system that gives optimum, reproducible recovery for the matrix/analyte combination to be measured. Suitable solvent choices are given in Table 1.

5.4.2 Methylene chloride:Acetone, $\text{CH}_2\text{Cl}_2:\text{CH}_3\text{COCH}_3$ (1:1, v:v). Pesticide quality or equivalent.

5.4.3 Methylene chloride, CH_2Cl_2 . Pesticide quality or equivalent.

5.4.4 Hexane, C_6H_{14} . Pesticide quality or equivalent.

5.5 Exchange solvents.

5.5.1 Hexane, C_6H_{14} . Pesticide quality or equivalent.

5.5.2 2-Propanol, $(CH_3)_2CHOH$. Pesticide quality or equivalent.

5.5.3 Cyclohexane, C_6H_{12} . Pesticide quality or equivalent.

5.5.4 Acetonitrile, CH_3CN . Pesticide quality or equivalent.

5.5.5 Methanol, CH_3OH . Pesticide quality or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample handling

7.1.1 Sediment/soil samples - Decant and discard any water layer on a sediment sample. Mix sample thoroughly, especially composited samples. Discard any foreign objects such as sticks, leaves, and rocks.

7.1.1.2 Determine the dry weight of the sample (Section 7.2) remaining after decanting. Measurement of soil pH may be required.

7.1.2 Waste samples - Samples consisting of multiphases must be prepared by the phase separation method in Chapter Two before extraction. This procedure is for solids only.

7.1.3 Dry waste samples amenable to grinding - Grind or otherwise subdivide the waste so that it either passes through a 1 mm sieve or can be extruded through a 1 mm hole. Introduce sufficient sample into the grinder to yield at least 100 g after grinding.

7.1.4 Gummy, fibrous or oily materials not amenable to grinding should be cut, shredded, or otherwise broken up to allow mixing, and maximum exposure of the sample surfaces for extraction. The professional judgment of the analyst is required for handling of these difficult matrices.

7.2 Determination of percent dry weight - In certain cases, sample results are desired based on a dry weight basis. When such data are desired, or required, a portion of sample for this determination should be weighed out at the same time as the portion used for analytical determination.

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

However, samples known or suspected to contain significant concentrations of toxic, flammable, or explosive constituents should not be overdried because of concerns for personal safety. Laboratory discretion is advised. It may be prudent to delay overdrying of the weighed-out portion until other analytical results are available.

7.2.1 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105°C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

7.3 Extraction method for samples expected to contain low concentrations of organics and pesticides (≤ 20 mg/kg):

7.3.1 The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400 mL beaker. Record the weigh to the nearest 0.1 g. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. If required, more sodium sulfate may be added. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks (see Method 3500 for details on the surrogate standard solution and the matrix spike solution). For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/ μ L of each base/neutral analyte and 200 ng/ μ L of each acid analyte in the extract to be analyzed (assuming a 1 μ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.3.2 Place the bottom surface of the tip of the #207 3/4 in. disrupter horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.3.3 Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse (pulsing energy rather than continuous energy) and percent-duty cycle knob set at 50% (energy on 50% of time and off 50% of time). Do not use microtip probe.

7.3.4 Decant and filter extracts through Whatman No. 41 filter paper (or equivalent) using vacuum filtration or centrifuge, and decant extraction solvent.

7.3.5 Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

7.3.6 Assemble a Kuderna-Danish (K-D) concentrator (if necessary) by attaching a 10 mL concentrator tube to a 500 mL evaporator flask. Transfer filtered extract to a 500 mL evaporator flask and proceed to the next section.

7.3.7 Add one to two clean boiling chips to the evaporation 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 (80-90 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.3.8 If a solvent exchange is required (as indicated in Table 1), momentarily remove the Snyder column, add 50 mL of the exchange solvent and a new boiling chip, and re-attach the Snyder column. Concentrate the extract as described in Section 7.3.8, raising the temperature of the water bath, if necessary, to maintain proper distillation. When the apparent volume again reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.3.9 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of methylene chloride or exchange solvent. If sulfur crystals are a problem, proceed to Method 3660 for cleanup. The extract may be further concentrated by using the technique outlined in Section 7.3.11 or adjusted to 10.0 mL with the solvent last used.

7.3.10 If further concentration is indicated in Table 1, either micro Snyder column technique (Section 7.3.11.1) or nitrogen blow down technique (Section 7.3.11.2) is used to adjust the extract to the final volume required.

7.3.10.1 Micro Snyder Column Technique

7.3.10.1.1 Add a clean boiling chip and attach a two ball micro Snyder column to the concentrator tube. Prewet the column by adding approximately 0.5 mL of methylene chloride or exchange solvent through the top. Place the apparatus in the hot water bath. Adjust the vertical position and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter,

but the chambers will not flood. When the liquid reaches an apparent volume of approximately 0.5 mL, remove the apparatus from the water bath and allow to drain and cool for at least 10 minutes. Remove the micro Snyder column and rinse its lower joint with approximately 0.2 mL of appropriate solvent and add to the concentrator tube. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.3.10.2 Nitrogen Blowdown Technique

7.3.10.2.1 Place the concentrator tube in a warm water bath (approximately 35 °C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.10.2.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost.

7.4 If analysis of the extract will not be performed immediately, stopper the concentrator tube and store refrigerated. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined cap and labeled appropriately.

7.5 Extraction method for samples expected to contain high concentrations of organics (> 20 mg/kg):

7.5.1 Transfer approximately 2 g (record weight to the nearest 0.1 g) of sample to a 20 mL vial. Wipe the mouth of the vial with a tissue to remove any sample material. Record the exact weight of sample taken. Cap the vial before proceeding with the next sample to avoid any cross contamination.

7.5.2 Add 2 g of anhydrous sodium sulfate to sample in the 20 mL vial and mix well.

7.5.3 Surrogate standards are added to all samples, spikes, and blanks (see Method 3500 for details on the surrogate standard solution and on the matrix spike solution). Add 2.0 mL of surrogate spiking solution to sample mixture. For the sample in each analytical batch selected for spiking, add 2.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds

should result in a final concentration of 200 ng/ μ L of each base/neutral analyte and 400 ng/ μ L of each acid analyte in the extract to be analyzed (assuming a 1 μ L injection). If Method 3640, Gel-Permeation Cleanup, is to be used, add twice the volume of surrogates and matrix spiking compounds since half the extract is lost due to loading of the GPC column.

7.5.4 Immediately add whatever volume of solvent is necessary to bring the final volume to 10.0 mL considering the added volume of surrogates and matrix spikes. Disrupt the sample with the 1/8 in. tapered microtip ultrasonic probe for 2 minutes at output control setting 5 and with mode switch on pulse and percent duty cycle at 50%. Extraction solvents are:

1. Nonpolar compounds (i.e., organochlorine pesticides and PCBs), hexane or appropriate solvent.
2. Extractable priority pollutants, methylene chloride.

7.5.5 Loosely pack disposable Pasteur pipets with 2 to 3 cm Pyrex glass wool plugs. Filter the extract through the glass wool and collect 5.0 mL in a concentrator tube if further concentration is required. Follow Section 7.3.11 for details on concentration. Normally, the 5.0 mL extract is concentrated to approximately 1.0 mL or less.

7.5.6 The extract is ready for cleanup or analysis, depending on the extent of interfering co-extractives.

8.0 QUALITY CONTROL

8.1 Any reagent blanks or matrix spike samples should be subject to exactly the same analytical procedures as those used on actual samples.

8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative method for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. U.S. EPA, Interlaboratory Comparison Study: Methods for Volatile and Semi-Volatile Compounds, Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV, EPA 600/4-84-027, 1984.

3. Christopher S. Hein, Paul J. Marsden, Arthur S. Shurtleff, "Evaluation of Methods 3540 (Soxhlet) and 3550 (Sonication) for Evaluation of Appendix IX Analytes form Solid Samples", S-CUBED, Report for EPA Contract 68-03-33-75, Work Assignment No. 03, Document No. SSS-R-88-9436, October 1988.

TABLE 1.
EFFICIENCY OF EXTRACTION SOLVENT SYSTEMS^a

Solvent System ^d			A		B		C		D		E	
Compound	CAS No. ^b	ABN ^c	%R	SD	%R	SD	%R	SD	%R	SD	%R	SD
4-Bromophenyl phenyl ether	101-55-3	N	64.2	6.5	56.4	0.5	86.7	1.9	84.5	0.4	73.4	1.0
4-Chloro-3-methylphenol	59-50-7	A	66.7	6.4	74.3	2.8	97.4	3.4	89.4	3.8	84.1	1.6
bis(2-Chloroethoxy)methane	111-91-1	N	71.2	4.5	58.3	5.4	69.3	2.4	74.8	4.3	37.5	5.8
bis(2-Chloroethyl) ether	111-44-4	N	42.0	4.8	17.2	3.1	41.2	8.4	61.3	11.7	4.8	1.0
2-Chloronaphthalene	91-58-7	N	86.4	8.8	78.9	3.2	100.8	3.2	83.0	4.6	57.0	2.2
4-Chlorophenyl phenyl ether	7005-72-3	N	68.2	8.1	63.0	2.5	96.6	2.5	80.7	1.0	67.8	1.0
1,2-Dichlorobenzene	95-50-1	N	33.3	4.5	15.8	2.0	27.8	6.5	53.2	10.1	2.0	1.2
1,3-Dichlorobenzene	541-73-1	N	29.3	4.8	12.7	1.7	20.5	6.2	46.8	10.5	0.6	0.6
Diethyl phthalate	84-66-2	N	24.8	1.6	23.3	0.3	121.1	3.3	99.0	4.5	94.8	2.9
4,6-Dinitro-o-cresol	534-52-1	A	66.1	8.0	63.8	2.5	74.2	3.5	55.2	5.6	63.4	2.0
2,4-Dinitrotoluene	121-14-2	N	68.9	1.6	65.6	4.9	85.6	1.7	68.4	3.0	64.9	2.3
2,6-Dinitrotoluene	606-20-2	N	70.0	7.6	68.3	0.7	88.3	4.0	65.2	2.0	59.8	0.8
Heptachlor epoxide	1024-57-3	N	65.5	7.8	58.7	1.0	86.7	1.0	84.8	2.5	77.0	0.7
Hexachlorobenzene	118-74-1	N	62.1	8.8	56.5	1.2	95.8	2.5	89.3	1.2	78.1	4.4
Hexachlorobutadiene	87-68-3	N	55.8	8.3	41.0	2.7	63.4	4.1	76.9	8.4	12.5	4.6
Hexachlorocyclopentadiene	77-47-4	N	26.8	3.3	19.3	1.8	35.5	6.5	46.6	4.7	9.2	1.7
Hexachloroethane	67-72-1	N	28.4	3.8	15.5	1.6	31.1	7.4	57.9	10.4	1.4	1.2
5-Nitro-o-toluidine	99-55-8	B	52.6	26.7	64.6	4.7	74.7	4.7	27.9	4.0	34.0	4.0
Nitrobenzene	98-95-3	N	59.8	7.0	38.7	5.5	46.9	6.3	60.6	6.3	13.6	3.2
Phenol	108-95-2	A	51.6	2.4	52.0	3.3	65.6	3.4	65.5	2.1	50.0	8.1
1,2,4-Trichlorobenzene	120-82-1	N	66.7	5.5	49.9	4.0	73.4	3.6	84.0	7.0	20.0	3.2

^a Percent recovery of analytes spiked at 200 mg/kg into NIST sediment SRM 1645

^b Chemical Abstracts Service Registry Number

^c Compound Type: A = Acid, B = Base, N = neutral

^d A = Methylene chloride

B = Methylene chloride/Acetone (1/1)

C = Hexane/Acetone (1/1)

D = Methyl t-butyl ether

E = Methyl t-butyl ether/Methanol (2/1)

TABLE 2.
SPECIFIC EXTRACTION CONDITIONS FOR VARIOUS DETERMINATIVE METHODS

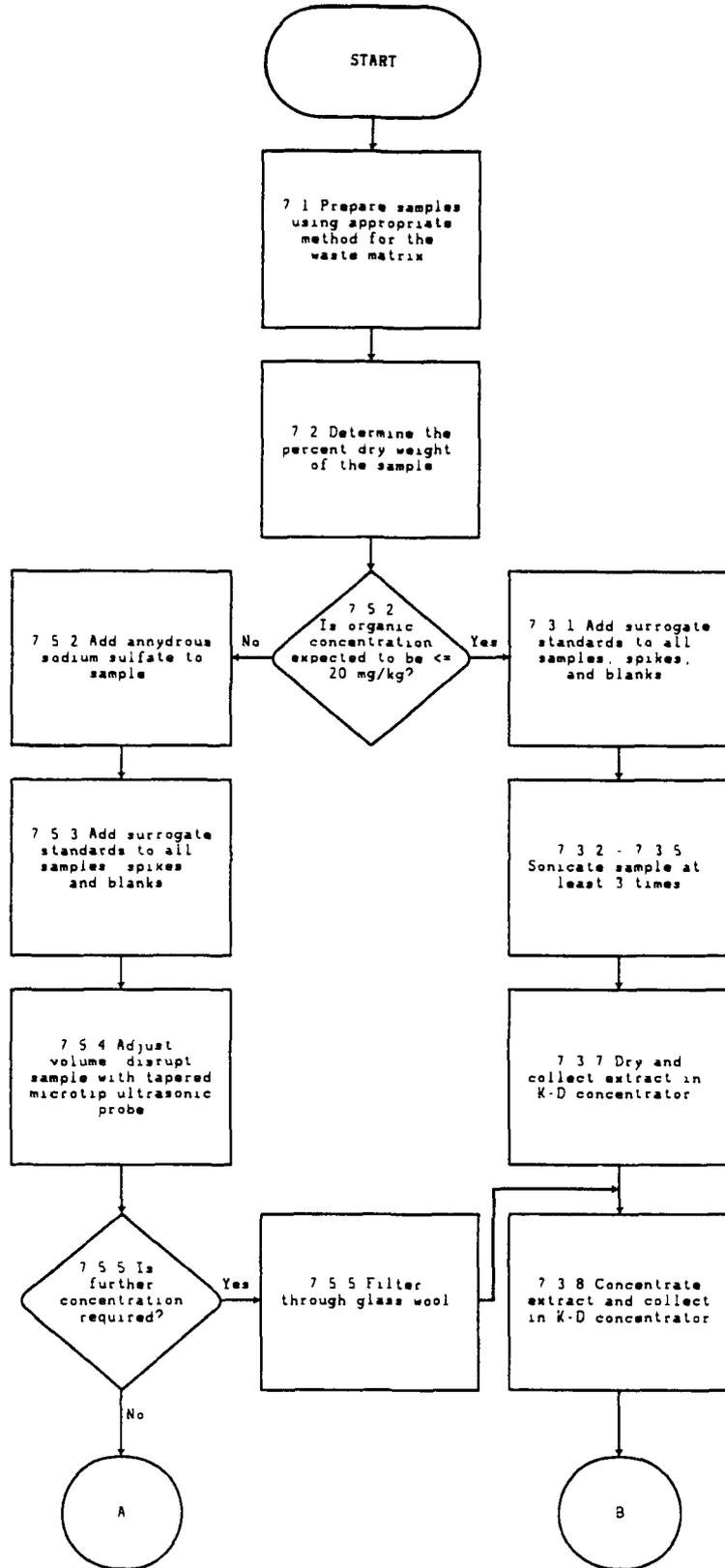
Determinative method	Extraction pH	Exchange solvent required for analysis	Exchange solvent required for cleanup	Volume of extract required for cleanup (mL)	Final extract volume for analysis (mL)
8040 ^a	as received	2-propanol	hexane	1.0	1.0, 10.0 ^b
8060	as received	hexane	hexane	2.0	10.0
8061	as received	hexane	hexane	2.0	10.0
8070	as received	methanol	methylene chloride	2.0	10.0
8080	as received	hexane	hexane	10.0	10.0
8081	as received	hexane	hexane	10.0	10.0
8090	as received	hexane	hexane	2.0	1.0
8100	as received	none	cyclohexane	2.0	1.0
8110	as received	hexane	hexane	2.0	10.0
8120	as received	hexane	hexane	2.0	1.0
8121	as received	hexane	hexane	2.0	1.0
8140	as received	hexane	hexane	10.0	10.0
8141	as received	hexane	hexane	10.0	10.0
8250 ^{a,c}	as received	none	--	--	1.0
8270 ^c	as received	none	--	--	1.0
8310	as received	acetonitrile	--	--	1.0
8321	as received	methanol	--	--	1.0
8410	as received	methylene chloride	methylene chloride	10.0	0.0 (dry)

^a To obtain separate acid and base/neutral extracts, Method 3650 should be performed following concentration of the extract to 10.0 mL.

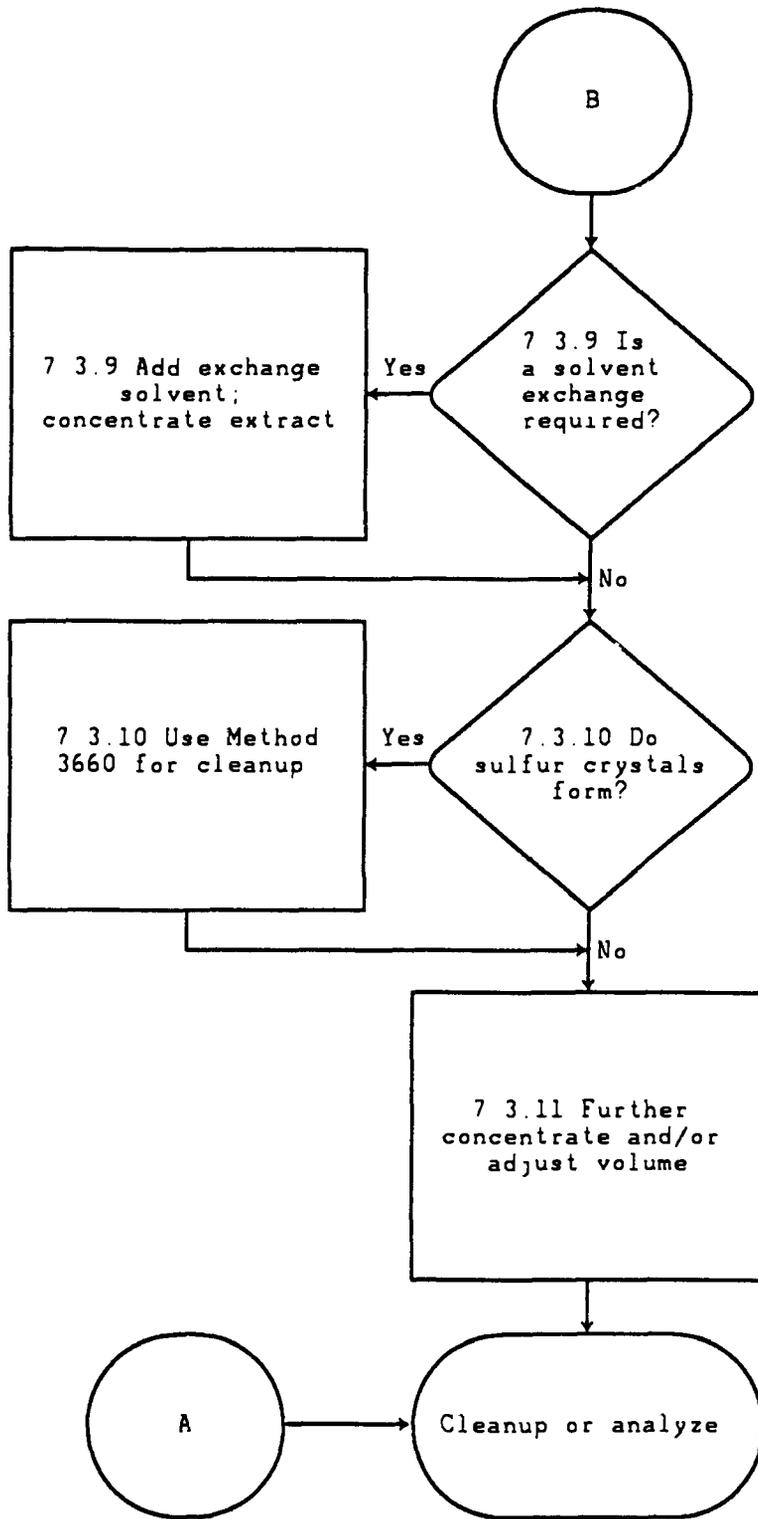
^b Phenols may be analyzed, by Method 8040, using a 1.0 mL 2-propanol extract by GC/FID. Method 8040 also contains an optical derivatization procedure for phenols which results in a 10 mL hexane extract to be analyzed by GC/ECD.

^c The specificity of GC/MS may make cleanup of the extracts unnecessary. Refer to Method 3600 for guidance on the cleanup procedures available if required.

METHOD 3550A
ULTRASONIC EXTRACTION



METHOD 3550A
continued



METHOD 5040A

ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST): GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 5040 was formerly Method 3720 in the Second Edition of this manual.

1.2 This method covers the determination of volatile principal organic hazardous constituents (POHCs), collected on Tenax and Tenax/charcoal sorbent cartridges using a volatile organic sampling train, VOST (1). Much of the description for purge-and-trap GC/MS analysis is described in Method 8240 of this chapter. Because the majority of gas streams sampled using VOST will contain a high concentration of water, the analytical method is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS. For the purposes of definition, volatile POHCs are those POHCs with boiling points less than 100°C.

1.3 This method is applicable to the analysis of Tenax and Tenax/charcoal cartridges used to collect volatile POHCs from wet stack gas effluents from hazardous waste incinerators.

1.4 The sensitivity of the analytical method for a particular volatile POHC depends on the level of interferences and the presence of detectable levels of volatile POHCs in blanks. The desired target detection limit of the analytical method is 0.1 ng/L (20 ng on a single pair of traps) for a particular volatile POHC desorbed from either a single pair of Tenax and Tenax/charcoal cartridges or by thermal desorption of up to six pairs of traps onto a single pair of Tenax and Tenax/charcoal traps. The resulting single pair of traps is then thermally desorbed and analyzed by purge-and-trap GC/MS.

1.5 This method is recommended for use only by experienced mass spectroscopists or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 A schematic diagram of the analytical system is shown in Figure 1. The contents of the sorbent cartridges are spiked with an internal standard and thermally desorbed for 10 min at 180°C with organic-free nitrogen or helium gas (at a flow rate of 40 mL/min), bubbled through 5 mL of organic-free reagent water, and trapped on an analytical adsorbent trap. After the 10 min. desorption, the analytical adsorbent trap is rapidly heated to 180°C, with the carrier gas flow reversed so that the effluent flow from the analytical trap is directed into the GC/MS. The volatile POHCs are separated by temperature programmed gas chromatography and detected by low-resolution mass spectrometry. The concentrations of volatile POHCs are calculated using the internal standard technique.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 and 8240.

4.0 APPARATUS AND MATERIALS

4.1 Thermal desorption unit:

4.1.1 The thermal desorption unit (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user-fabricated unit is required) should be capable of thermally desorbing the sorbent resin tubes. It should also be capable of heating the tubes to $180 \pm 10^{\circ}\text{C}$ with flow of organic-free nitrogen or helium through the tubes.

4.2 Purge-and-trap unit:

4.2.1 The purge-and-trap unit consists of three separate pieces of equipment: the sample purger, trap, and the desorber. It should be capable of meeting all requirements of Method 5030 for analysis of purgeable organic compounds from water.

4.3 GC/MS system: As described in Method 8240.

5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - Pesticide grade, or equivalent.

5.3 Analytical trap reagents:

5.3.1 2,6-Diphenylene oxide polymer: Tenax (60/80 mesh), chromatographic grade or equivalent.

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

5.3.3 Silica gel: Davison Chemical (35/00 mesh), Grade 15, or equivalent.

5.3.4 Charcoal: Petroleum-based (SKC Lot 104 or equivalent).

5.4 Stock standard solution:

5.4.1 Stock standard solutions will be prepared from pure standard materials or purchased as certified solutions. The stock standards should be prepared in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic

gas respirator should be used when the analyst handles high concentrations of such materials.

5.4.2 Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of $<35^{\circ}\text{C}$. All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards:

5.5.1 Using stock standard solutions, prepare, in methanol, secondary dilution standards that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the desorbed calibration standards will bracket the working range of the analytical system.

5.6 4-Bromofluorobenzene (BFB) standard:

5.6.1 Prepare a 25 ng/ μL solution of BFB in methanol.

5.7 Deuterated benzene:

5.7.1 Prepare a 25 ng/ μL solution of benzene- d_6 in methanol.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 0030, Chapter Ten.

6.2 Sample trains obtained from the VOST should be analyzed within 2-6 weeks of sample collection.

7.0 PROCEDURE

7.1 Assembly of PTD device:

7.1.1 Assemble a purge-and-trap desorption device (PTD) that meets all the requirements of Method 5030 (refer to Figure 1).

7.1.2 Connect the thermal desorption device to the PTD device. Calibrate the PTD-GC/MS system using the internal standard technique.

7.2 Internal standard calibration procedure:

7.2.1 This approach requires the use of deuterated benzene as the internal standard for these analyses. Other internal standards may be proposed for use in certain situations. The important criteria for choosing a particular compound as an internal standard are that it be similar in analytical behavior to the compounds of interest and that it can be demonstrated that the measurement of the internal standard be unaffected by method or matrix interferences. Other internal standards that have been used are d_{10} -ethylbenzene and d_4 -1,2-dichloroethane. One adds 50 ng of BFB to all sorbent cartridges (in addition to one or more

internal standards) to provide continuous monitoring of the GC/MS performance relative to BFB.

7.2.2 Prepare calibration standards at a minimum of three concentration levels for each analyte of interest.

7.2.3 The calibration standards are prepared by spiking a blank Tenax or Tenax/charcoal trap with a methanolic solution of the calibration standards (including 50 ng of the internal standard, such as deuterated benzene), using the flash evaporation technique. The flash evaporation technique requires filling the needle of a 5.0 μL syringe with clean methanol and drawing air into the syringe to the 1.0 μL mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 $\mu\text{g}/\mu\text{L}$ of the internal standard) to the 2.0 μL mark. The glass traps should be attached to the injection port of a gas chromatograph while maintaining the injector temperature at 160°C. The carrier gas flow through the traps should be maintained at about 50 mL/min.

7.2.4 After directing the gas flow through the trap, the contents of the syringe should be slowly expelled through the gas chromatograph injection port over about 15 sec. After 25 sec have elapsed, the gas flow through the trap should be shut off, the syringe removed, and the trap analyzed by the PTD-GC/MS procedure outlined in Method 8240. The total flow of gas through the traps during addition of calibration standards to blank cartridges, or internal standards to sample cartridges, should be 25 mL or less.

7.2.5 Analyze each calibration standard for both Tenax and Tenax/charcoal cartridges according to Section 7.3. Tabulate the area response of the characteristic ions of each analyte against the concentration of the internal standard and calculate the response factor (RF) for each compound, using Equation 1.

$$\text{RF} = A_s C_{is} / A_{is} C_s \quad (1)$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area of the characteristic ion for the internal standard.

C_{is} = Amount (ng) of the internal standard.

C_s = Amount (ng) of the volatile POHC in calibration standard.

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

7.2.6 The working calibration curve or RF must be verified on each working day by the measurement of one or more of the calibration standards. If the response varies by more than $\pm 25\%$ for any analyte, a new calibration standard must be prepared and analyzed for that analyte.

7.3 The schematic of the PTD-GC/MS system is shown in Figure 1. The sample cartridge is placed in the thermal desorption apparatus (for Inside/Inside VOST cartridges, use Supelco "clamshell" heater; for Inside/Outside VOST cartridges, user fabricated unit is required) and desorbed in the purge-and-trap system by heating to 180°C for 10 min at a flow rate of 40 mL/min. The desorbed components pass into the bottom of the water column, are purged from the water, and collected on the analytical adsorbent trap. After the 10 min desorption period, the compounds are desorbed from the analytical adsorbent trap into the GC/MS system according to the procedures described in Method 8240.

7.4 Qualitative analysis

7.4.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.4.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine, where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time, will be accepted as meeting this criterion.

7.4.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.4.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.4.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.4.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas

chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.4.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of the sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.5 Quantitative analysis

7.5.1 When an analyte has been qualitatively identified, quantitation should be based on the integrated abundance from the EICP of the primary characteristic ion chosen for that analyte. If the sample produces an interference for the primary characteristic ion, a secondary characteristic ion should be used.

7.5.1.1 Using the internal standard calibration procedure, the amount of analyte in the sample cartridge is calculated using the response factor (RF) determined in Section 7.2.5 and Equation 2.

$$\text{Amount of POHC} = A_s C_{is} / A_{is} RF \quad (2)$$

where:

A_s = Area of the characteristic ion for the analyte to be measured.

A_{is} = Area for the characteristic ion of the internal standard.

C_{is} = Amount (ng) of internal standard.

7.5.1.2 The choice of methods for evaluating data collected using VOST for incinerator trial burns is a regulatory decision. The procedures used extensively by one user are outlined below.

7.5.1.3 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.5.1.4 The observation of high concentrations of POHCs of interest in blank cartridges indicates possible residual contamination of the sorbent cartridges prior to shipment to and use at the site. Data that fall in this category (especially data indicating high concentrations of POHCs in blank sorbent cartridges) should be qualified with regard to validity, and blank data should be reported separately. The applicability of data of this type to the determination of DRE is a regulatory decision. Continued observation of high concentrations of POHCs in blank sorbent cartridges indicates that procedures for cleanup, monitoring, shipment, and storage of sorbent cartridges by a particular user be investigated to eliminate this problem.

7.5.1.5 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 0030 for sample preparation procedures.

8.2 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of blank Tenax and Tenax/charcoal cartridges spiked with the analytes of interest. The laboratory is required to maintain performance records to define the quality of data that are generated. Ongoing performance checks must be compared with

established performance criteria to determine if results are within the expected precision and accuracy limits of the method.

8.2.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 7.2.

8.2.2 The laboratory must spike all Tenax and Tenax/charcoal cartridges with the internal standard(s) to monitor continuing laboratory performance. This procedure is described in Section 7.2.

8.3 To establish the ability to generate acceptable accuracy and precision, the analyst must spike blank Tenax and Tenax/charcoal cartridges with the analytes of interest at two concentrations in the working range.

8.3.1 The average response factor (R) and the standard deviation (S) for each must be calculated.

8.3.2 The average recovery and standard deviation must fall within the expected range for determination of volatile POHCs using this method. The expected range for recovery of volatile POHCs using this method is 50-150%.

8.4 The analyst must calculate method performance criteria for the internal standard(s).

8.4.1 Calculate upper and lower control limits for method performances using the average area response (A) and standard deviation(s) for internal standard:

$$\text{Upper Control Limit (UCL)} = A + 3S$$

$$\text{Lower Control Limit (LCL)} = A - 3S$$

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance. The control limits must be replaced by method performance criteria as they become available from the U.S. EPA.

8.5 The laboratory is required to spike all sample cartridges (Tenax and Tenax/charcoal) with internal standard.

8.6 Each day, the analyst must demonstrate through analysis of blank Tenax and Tenax/charcoal cartridges and organic-free reagent water that interferences from the analytical system are under control.

8.7 The daily GC/MS performance tests required for this method are described in Method 8240.

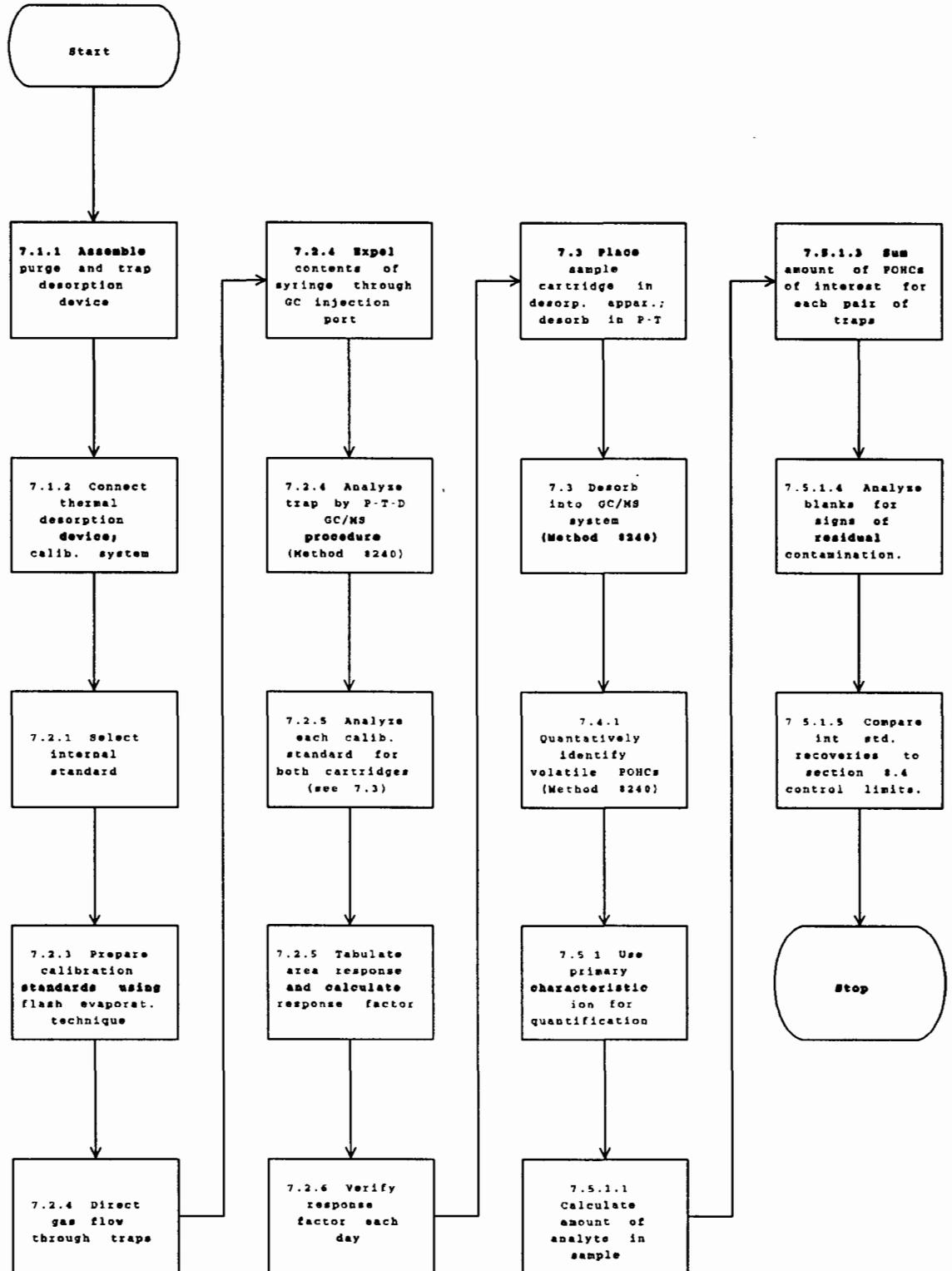
9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

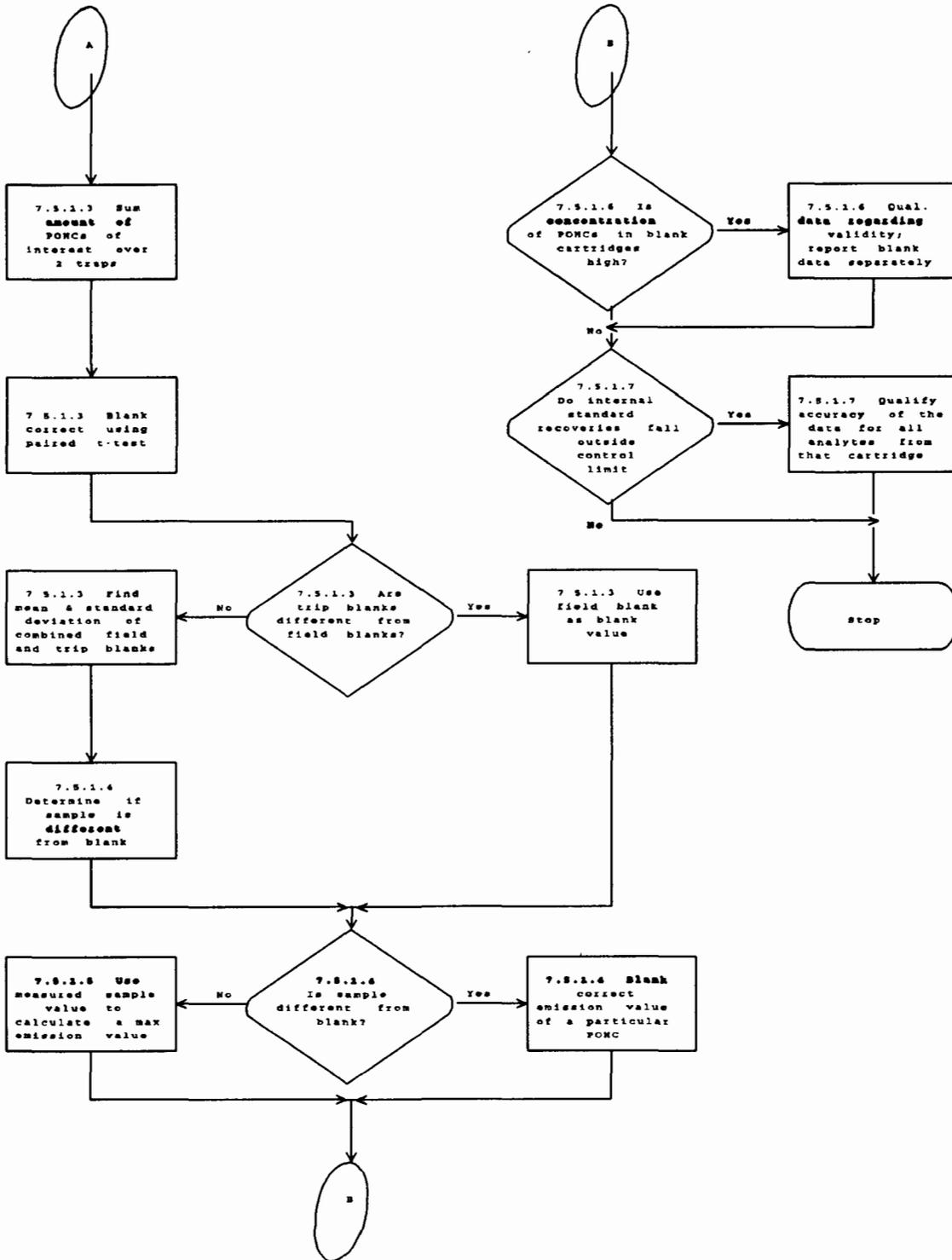
10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA/600/8-84-007, March 1984.
2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014a, January 1986.

METHOD 5040A
ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN (VOST):
GAS CHROMATOGRAPHY/MASS SPECTROMETRY TECHNIQUE



METHOD 5040A
continued



METHOD 5041

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC
SAMPLING TRAIN: WIDE-BORE CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 This method describes the analysis of volatile principal organic hazardous constituents (POHCs) collected from the stack gas effluents of hazardous waste incinerators using the VOST methodology (1). For a comprehensive description of the VOST sampling methodology see Method 0030. The following compounds may be determined by this method:

Compound Name	CAS No. ^a
Acetone	67-64-1
Acrylonitrile	107-13-1
Benzene	71-43-2
Bromodichloromethane	75-27-4
Bromoform ^b	75-25-2
Bromomethane ^c	74-83-9
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chlorodibromomethane	124-48-1
Chloroethane ^c	75-00-3
Chloroform	67-66-3
Chloromethane ^c	74-87-3
Dibromomethane	74-95-3
1,1-Dichloroethane	75-35-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
cis-1,3-Dichloropropene	10061-01-5
trans-1,3-Dichloropropene	10061-02-6
Ethylbenzene ^b	100-41-4
Iodomethane	74-88-4
Methylene chloride	75-09-2
Styrene ^b	100-42-5
1,1,2,2-Tetrachloroethane ^b	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
1,1,2-Trichloroethane	79-00-5
Trichloroethene	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane ^b	96-18-4
Vinyl chloride ^c	75-01-4
Xylenes ^b	

^a Chemical Abstract Services Registry Number.

^b Boiling point of this compound is above 132°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

^c Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Section 1.3 for discussion.

1.2 This method is most successfully applied to the analysis of non-polar organic compounds with boiling points between 30°C and 100°C. Data are applied to the calculation of destruction and removal efficiency (DRE), with limitations discussed below.

1.3 This method may be applied to analysis of many compounds which boil above 100°C, but Method 0030 is always inappropriate for collection of compounds with boiling points above 132°C. All target analytes with boiling points greater than 132°C are so noted in the target analyte list presented in Section 1.1. Use of Method 0030 for collection of compounds boiling between 100°C and 132°C is often possible, and must be decided based on case by case inspection of information such as sampling method collection efficiency, tube desorption efficiency, and analytical method precision and bias. An organic compound with a boiling point below 30°C may break through the sorbent under the conditions used for sample collection. Quantitative values obtained for compounds with boiling points below 30°C must be qualified, since the value obtained represents a minimum value for the compound if breakthrough has occurred. In certain cases, additional QC measures may have been taken during sampling very low boilers with Method 0030. This information should be considered during the data interpretation stage.

When Method 5041 is used for survey analyses, values for compounds boiling above 132°C may be reported and qualified since the quantity obtained represents a minimum value for the compound. These minimum values should not be used for trial burn DRE calculations or to prove insignificant risk.

1.4 The VOST analytical methodology can be used to quantitate volatile organic compounds that are insoluble or slightly soluble in water. When volatile, water soluble compounds are included in the VOST organic compound analyte list, quantitation limits can be expected to be approximately ten times higher than quantitation limits for water insoluble compounds (if the compounds can be recovered at all) because the purging efficiency from water (and possibly from Tenax-GC®) is poor.

1.5 Overall sensitivity of the method is dependent upon the level of interferences encountered in the sample and the presence of detectable concentrations of volatile POHCs in blanks. The target detection limit of this method is 0.1 $\mu\text{g}/\text{m}^3$ (ng/L) of flue gas, to permit calculation of a DRE equal to or greater than 99.99% for volatile POHCs which may be present in the waste stream at 100 ppm. The upper end of the range of applicability of this method is limited by the dynamic range of the analytical instrumentation, the overall loading of organic compounds on the exposed tubes, and breakthrough of the volatile POHCs on the sorbent traps used to collect the sample. Table 1 presents

retention times and characteristic ions for volatile compounds which can be determined by this method. Table 2 presents method detection limits for a range of volatile compounds analyzed by the wide-bore VOST methodology.

1.6 The wide-bore VOST analytical methodology is restricted to use by, or under the supervision of, analysts experienced in the use of sorbent media, purge-and-trap systems, and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The sorbent tubes are thermally desorbed by heating and purging with organic-free helium. The gaseous effluent from the tubes is bubbled through pre-purged organic-free reagent water and trapped on an analytical sorbent trap in a purge-and-trap unit (Figure 2). After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore column under subambient conditions. The volatile organic compounds desorbed from the analytical trap are separated by temperature programmed high resolution gas chromatography and detected by continuously scanning low resolution mass spectrometry (Figure 3). Concentrations of volatile organic compounds are calculated from a multi-point calibration curve, using the method of response factors.

3.0 INTERFERENCES

3.1 Sorbent tubes which are to be analyzed for volatile organic compounds can be contaminated by diffusion of volatile organic compounds (particularly Freon® refrigerants and common organic solvents) through the external container (even through a Teflon® lined screw cap on a glass container) and the Swagelok® sorbent tube caps during shipment and storage. The sorbent tubes can also be contaminated if organic solvents are present in the analytical laboratory. The use of blanks is essential to assess the extent of any contamination. Field blanks must be prepared and taken to the field. The end caps of the tubes are removed for the period of time required to exchange two pairs of traps on the VOST sampling apparatus. The tubes are recapped and shipped and handled exactly as the actual field samples are shipped and handled. At least one pair of field blanks is included with each six pairs of sample cartridges collected.

3.2 At least one pair of blank cartridges (one Tenax-GC®, one Tenax-GC®/charcoal) shall be included with shipment of cartridges to a hazardous waste incinerator site as trip blanks. These trip blanks will be treated like field blanks except that the end caps will not be removed during storage at the site. This pair of traps will be analyzed to monitor potential contamination which may occur during storage and shipment.

3.3 Analytical system blanks are required to demonstrate that contamination of the purge-and-trap unit and the gas chromatograph/mass spectrometer has not occurred or that, in the event of analysis of sorbent tubes with very high concentrations of organic compounds, no compound carryover is occurring. Tenax® from the same preparation batch as the Tenax® used for field

sampling should be used in the preparation of the method (laboratory) blanks. A sufficient number of cleaned Tenax® tubes from the same batch as the field samples should be reserved in the laboratory for use as blanks.

3.4 Cross contamination can occur whenever low-concentration samples are analyzed after high-concentration samples, or when several high-concentration samples are analyzed sequentially. When an unusually concentrated sample is analyzed, this analysis should be followed by a method blank to establish that the analytical system is free of contamination. If analysis of a blank demonstrates that the system is contaminated, an additional bake cycle should be used. If the analytical system is still contaminated after additional baking, routine system maintenance should be performed: the analytical trap should be changed and conditioned, routine column maintenance should be performed (or replacement of the column and conditioning of the new column, if necessary), and bakeout of the ion source (or cleaning of the ion source and rods, if required). After system maintenance has been performed, analysis of a blank is required to demonstrate that the cleanliness of the system is acceptable.

3.5 Impurities in the purge gas and from organic compounds out-gassing in tubing 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 analyzing two sets of clean, blank sorbent tubes with organic-free reagent purge water as system blanks. The analytical system is acceptably clean when these two sets of blank tubes show values for the analytes which are within one standard deviation of the normal system blank. Use of plastic coatings, non-Teflon® thread sealants, or flow controllers with rubber components should be avoided.

3.6 VOST tubes are handled in the laboratory to spike standards and to position the tubes within the desorption apparatus. When sorbent media are handled in the laboratory atmosphere, contamination is possible if there are organic solvents in use anywhere in the laboratory. It is therefore necessary to make daily use of system blanks to monitor the cleanliness of the sorbents and the absence of contamination from the analytical system. A single set of system blank tubes shall be exposed to normal laboratory handling procedures and analyzed as a sample. This sample should be within one standard deviation of normal VOST tube blanks to demonstrate lack of contamination of the sorbent media.

3.7 If the emission source has a high concentration of non-target organic compounds (for example, hydrocarbons at concentrations of hundreds of ppm), the presence of these non-target compounds will interfere with the performance of the VOST analytical methodology. If one or more of the compounds of interest saturates the chromatographic and mass spectrometric instrumentation, no quantitative calculations can be made and the tubes which have been sampled under the same conditions will yield no valid data for any of the saturated compounds. In the presence of a very high organic loading, even if the compounds of interest are not saturated, the instrumentation is so saturated that the linear range has been surpassed. When instrument saturation occurs, it is possible that compounds of interest cannot even be identified correctly because a saturated mass spectrometer may mis-assign masses. Even if compounds of interest can be identified, accurate quantitative calculations are impossible at detector saturation. No determination can be made at detector saturation, even if the target compound itself is not saturated. At detector saturation, a negative bias

will be encountered in analytical measurements and no accurate calculation can be made for the Destruction and Removal Efficiency if analytical values may be biased negatively.

3.8 The recoveries of the surrogate compounds, which are spiked on the VOST tubes immediately before analysis, should be monitored carefully as an overall indicator of the performance of the methodology. Since the matrix of stack emissions is so variable, only a general guideline for recovery of 50-150% can be used for surrogates. The analyst cannot use the surrogate recoveries as a guide for correction of compound recoveries. The surrogates are valuable only as a general indicator of correct operation of the methodology. If surrogates are not observed or if recovery of one or more of the surrogates is outside the 50-150% range, the VOST methodology is not operating correctly. The cause of the failure in the methodology is not obvious. The matrix of stack emissions contains large amounts of water, may be highly acidic, and may contain large amounts of target and non-target organic compounds. Chemical and surface interactions may be occurring on the tubes. If recoveries of surrogate compounds are extremely low or surrogate compounds cannot even be identified in the analytical process, then failure to observe an analyte may or may not imply that the compound of interest has been removed from the emissions with a high degree of efficiency (that is, the Destruction and Removal Efficiency for that analyte is high).

4.0 APPARATUS AND MATERIALS

4.1 Tube desorption apparatus: Acceptable performance of the methodology requires: 1) temperature regulation to ensure that tube temperature during desorption is regulated to $180^{\circ}\text{C} \pm 10^{\circ}$; 2) good contact between tubes and the heating apparatus to ensure that the sorbent bed is thoroughly and uniformly heated to facilitate desorption of organic compounds; and 3) gas-tight connections to the ends of the tubes to ensure flow of desorption gas through the tubes without leakage during the heating/desorption process. A simple clamshell heater which will hold tubes which are 3/4" in outer diameter will perform acceptably as a desorption apparatus.

4.2 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: a sample purge vessel, an analytical trap, and a desorber. Complete devices are commercially available from a variety of sources, or the separate components may be assembled. The cartridge thermal desorption apparatus is connected to the sample purge vessel by 1/8" Teflon® tubing (unheated transfer line). The tubing which connects the desorption chamber to the sample purge vessel should be as short as is practical.

4.2.1 The sample purge vessel is required to hold 5 mL of organic-free reagent water, through which the gaseous effluent from the VOST tubes is routed. The water column should be at least 3 cm deep. The gaseous headspace between the water column and the analytical trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The sample purger shown in Figure 4 meets these requirements. Alternate sample purging vessels may be used if equivalent performance is demonstrated.

4.2.2 The analytical trap must be at least 25 cm and have an internal diameter of at least 0.105 in. The analytical trap must contain the following components:

2,6-diphenylene oxide polymer:	60/80 mesh, chromatograph grade (Tenax-GC®, or equivalent)
methyl silicone packing:	OV-1 (3%) on Chromosorb-W 60/80 mesh, or equivalent
silica gel:	35/60 mesh, Davison grade 15 or equivalent
coconut charcoal:	prepare from Barneby Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

The proportions are: 1/3 Tenax-GC®, 1/3 silica gel, and 1/3 charcoal, with approximately 1.0 cm of methyl silicone packing. The analytical trap should be conditioned for four hours at 180°C with gas flow (10 mL/min) prior to use in sample analysis. During conditioning, the effluent of the trap should not be vented to the analytical column. The thermal desorption apparatus is connected to the injection system of the mass spectrometer by a transfer line which is heated to 100°C.

4.2.3 The desorber must be capable of rapidly heating the analytical trap to 180°C for desorption. The polymer section of the trap should not exceed 180°C, and the remaining sections should not exceed 220°C, during bake-out mode.

4.3 Gas chromatograph/mass spectrometer/data system:

4.3.1 Gas chromatograph: An analytical system complete with a temperature programmable oven with sub-ambient temperature capabilities and all required accessories, including syringes, analytical columns, and gases.

4.3.2 Chromatographic column: 30 m x 0.53 mm ID wide-bore fused silica capillary column, 3 µm film thickness, DB-624 or equivalent.

4.3.3 Mass spectrometer: capable of scanning from 35-260 amu every second or less, using 70 eV (nominal) electron energy in the electron ionization mode and producing a mass spectrum that meets all of the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) is injected into the water in the purge vessel.

4.3.4 Gas chromatograph/mass spectrometer interface: Any gas chromatograph to mass spectrometer interface that gives acceptable calibration points at 50 ng or less per injection of each of the analytes, and achieves the performance criteria for 4-bromofluorobenzene shown in Table 3, may be used. If a glass jet separator is used with the wide-bore

column, a helium make-up flow of approximately 15 mL, introduced after the end of the column and prior to the entrance of the effluent to the separator, will be required for optimum performance.

4.3.5 Data system: A computer system that allows the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any gas chromatographic/mass spectrometric data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows the integration of the ion abundances in any EICP between specified time or scan number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.4 Wrenches: 9/16", 1/2", 7/16", and 5/16".

4.5 Teflon® tubing: 1/8" diameter.

4.6 Syringes: 25 µL syringes (2), 10 µL syringes (2).

4.7 Fittings: 1/4" nuts, 1/8" nuts, 1/16" nuts, 1/4" to 1/8" union, 1/4" to 1/4" union, 1/4" to 1/16" union.

4.8 Adjustable stand to raise the level of the desorption unit, if required.

4.9 Volumetric flasks: 5 mL, class A with ground glass stopper.

4.10 Injector port or equivalent, heated to 180°C for loading standards onto VOST tubes prior to analysis.

4.11 Vials: 2 mL, with Teflon® lined screw caps or crimp tops.

4.12 Syringe: 5 mL, gas-tight with shutoff valve.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.1 It is advisable to maintain the stock of organic-free reagent water generated for use in the purge-and-trap apparatus with a continuous

stream of inert gas bubbled through the water. Continuous bubbling of the inert gas maintains a positive pressure of inert gas above the water as a safeguard against contamination.

5.3 Methanol, CH_3OH . Pesticide quality or equivalent. To avoid contamination with other laboratory solvents, it is advisable to maintain a separate stock of methanol for the preparation of standards for VOST analysis and to regulate the use of this methanol very carefully.

5.4 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable. Stock standard solutions must be prepared in high purity methanol. All preparation of standards should take place in a hood, both to avoid contamination and to ensure safety of the analyst preparing the standards.

5.4.1 Place about 4 mL of high purity methanol in a 5 mL volumetric flask. Allow the flask to stand, unstoppered, for about 10 min, or until all alcohol wetted surfaces have dried.

5.4.1.1 Add appropriate volumes of neat liquid chemicals or certified solutions, using a syringe of the appropriate volume. Liquid which is added to the volumetric flask must fall directly into the alcohol without contacting the neck of the flask. Gaseous standards can be purchased as methanol solutions from several commercial vendors.

5.4.1.2 Dilute to volume with high purity methanol, stopper, and then mix by inverting the flask several times. Calculate concentration by the dilution of certified solutions or neat chemicals.

5.4.2 Transfer the stock standard solution into a Teflon® sealed screw cap bottle. An amber bottle may be used. Store, with minimal headspace, at -10°C to -20°C , and protect from light.

5.4.3 Prepare fresh standards every two months for gases. Reactive compounds such as styrene may need to be prepared more frequently. All other standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards: Using stock standard solutions, prepare, in high purity methanol, secondary dilution standards containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Surrogate standards: The recommended surrogates are toluene- d_8 , 4-bromofluorobenzene, and 1,2-dichloroethane- d_4 . Other compounds may be used as surrogate compounds, depending upon the requirements of the analysis. Surrogate compounds are selected to span the elution range of the compounds of interest.

Isotopically labeled compounds are selected to preclude the observation of the same compounds in the stack emissions. More than one surrogate is used so that surrogate measurements can still be made even if analytical interferences with one or more of the surrogate compounds are encountered. However, at least three surrogate compounds should be used to monitor the performance of the methodology. A stock surrogate compound solution in high purity methanol should be prepared as described in Section 5.4, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 $\mu\text{g}/10\text{ mL}$ in high purity methanol. Each pair of VOST tubes (or each individual VOST tube, if the tubes are analyzed separately) must be spiked with 10 μL of the surrogate spiking solution prior to GC/MS analysis.

5.7 Internal standards: The recommended internal standards are bromochloromethane, 1,4-difluorobenzene, and chlorobenzene- d_5 . Other compounds may be used as internal standards as long as they have retention times similar to the compounds being analyzed by GC/MS. The internal standards should be distributed through the chromatographic elution range. Prepare internal standard stock and secondary dilution standards in high purity methanol using the procedures described in Sections 5.2 and 5.3. The secondary dilution standard should be prepared at a concentration of 25 mg/L of each of the internal standard compounds. Addition of 10 μL of this internal standard solution to each pair of VOST tubes (or to each VOST tube, if the tubes are analyzed individually) is the equivalent of 250 ng total.

5.8 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/ μL of BFB in high purity methanol should be prepared for use as a tuning standard.

5.9 Calibration standards: Calibration standards at a minimum of five concentrations will be required from the secondary dilution of stock standards (see Sections 5.2 and 5.3). A range of concentrations for calibration can be obtained by use of different volumes of a 50 mg/L methanol solution of the calibration standards. One of the concentrations used should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in field samples but should not exceed the linear range of the GC/MS analytical system (a typical range for a calibration would be 10, 50, 100, 350, and 500 ng, for example). Each calibration standard should contain each analyte for detection by this method. Store calibration standards for one week only in a vial with no headspace.

5.10 Great care must be taken to maintain the integrity of all standard solutions. All standards of volatile compounds in methanol must be stored at -10° to -20°C in amber bottles with Teflon[®] lined screw caps or crimp tops. In addition, careful attention must be paid to the use of syringes designated for a specific purpose or for use with only a single standard solution since cross contamination of volatile organic standards can occur very readily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Method 0030 for the VOST Sampling Methodology.

6.2 VOST samples are collected on paired cartridges. The first of the pair of sorbent cartridges is packed with approximately 1.6 g of Tenax-GC® resin. The second cartridge of the pair is packed with Tenax-GC® and petroleum based charcoal (3:1 by volume; approximately 1 g of each). In sampling, the emissions gas stream passes through the Tenax-GC® layer first and then through the charcoal layer. The Tenax-GC® is cleaned and reused; charcoal is not reused when tubes are prepared. Sorbent is cleaned and the tubes are packed. The tubes are desorbed and subjected to a blank check prior to being sent to the field. When the tubes are used for sampling (see Figure 5 for a schematic diagram of the Volatile Organic Sampling Train (VOST)), cooling water is circulated to the condensers and the temperature of the cooling water is maintained near 0°C. The end caps of the sorbent cartridges are placed in a clean, screw capped glass container during sample collection.

6.3 After the apparatus is leak checked, sample collection is accomplished by opening the valve to the first condenser, turning on the pump, and sampling at a rate of 1 liter/min for 20 minutes. The volume of sample for any pair of traps should not exceed 20 liters. An alternative set of conditions for sample collection requires sampling at a reduced flow rate, where the overall volume of sample collected is 5 liters at a rate of 0.25 L/min for 20 minutes. The 20 minute period is required for collecting an integrated sample.

6.4 Following collection of 20 liters of sample, the train is leak checked a second time at the highest pressure drop encountered during the run to minimize the chance of vacuum desorption of organics from the Tenax®.

6.5 The train is returned to atmospheric pressure and the two sorbent cartridges are removed. The end caps are replaced and the cartridges are placed in a suitable environment for storage and transport until analysis. The sample is considered invalid if the leak test does not meet specifications.

6.6 A new pair of cartridges is placed in the VOST, the VOST is leak checked, and the sample collection process is repeated until six pairs of traps have been exposed.

6.7 All sample cartridges are kept in coolers on cold packs after exposure and during shipment. Upon receipt at the laboratory, the cartridges are stored in a refrigerator at 4°C until analysis.

7.0 PROCEDURE

7.1 Recommended operating conditions for cartridge desorber, purge-and-trap unit, and gas chromatograph/mass spectrometer using the wide-bore column are:

<u>Cartridge Desorption Oven</u>	
Desorb Temperature	180°C
Desorb Time	11 minutes
Desorption Gas Flow	40 mL/min
Desorption/Carrier Gas	Helium, Grade 5.0

Purge-and-Trap Concentrator

Analytical Trap Desorption Flow	2.5 mL/min helium
Purge Temperature	Ambient
Purge Time	11 minutes
Analytical Trap Desorb Temperature	180°C
Analytical Trap Desorb Time	5 minutes

Gas Chromatograph

Column	DB-624, 0.53 mm ID x 30 m thick film (3 μ m) fused silica capillary, or equivalent
Carrier Gas Flow	15 mL/min
Makeup Gas Flow	15 mL/min
Injector Temperature	200°C
Transfer Oven Temperature	240°C
Initial Temperature	5°C
Initial Hold Time	2 minutes
Program Rate	6°C/min
Final Temperature	240°C
Final Hold Time	1 minute, or until elution ceases

Mass Spectrometer

Manifold Temperature	105°C
Scan Rate	1 sec/cycle
Mass Range	35-260 amu
Electron Energy	70 eV (nominal)
Source Temperature	According to manufacturer's specifications

7.2 Each GC/MS system must be hardware tuned to meet the criteria in Table 3 for a 50 ng injection of 4-bromofluorobenzene (2 μ L injection of the BFB standard solution into the water of the purge vessel). No analyses may be initiated until the criteria presented in Table 3 are met.

7.3 Assemble a purge-and-trap device that meets the specifications in Method 5030. Condition the analytical trap overnight at 180°C in the purge mode, with an inert gas flow of at least 20 mL/min. Prior to use each day, condition the trap for 10 minutes by backflushing at 180°C, with the column at 220°C.

7.4 Connect the purge-and-trap device to a gas chromatograph.

7.5 Assemble a VOST tube desorption apparatus which meets the requirements of Section 4.1.

7.6 Connect the VOST tube desorption apparatus to the purge-and-trap unit.

7.7 Calibrate the instrument using the internal standard procedure, with standards and calibration compounds spiked onto cleaned VOST tubes for calibration.

7.7.1 Compounds in methanolic solution are spiked onto VOST tubes using the flash evaporation technique. To perform flash evaporation, the

injector of a gas chromatograph or an equivalent piece of equipment is required.

7.7.1.1 Prepare a syringe with the appropriate volume of methanolic standard solution (either surrogates, internal standards, or calibration compounds).

7.7.1.2 With the injector port heated to 180°C, and with an inert gas flow of 10 mL/min through the injector port, connect the paired VOST tubes (connected as in Figure 1, with gas flow in the same direction as the sampling gas flow) to the injector port; tighten with a wrench so that there is no leakage of gas. If separate tubes are being analyzed, an individual Tenax® or Tenax®/charcoal tube is connected to the injector.

7.7.1.3 After directing the gas flow through the VOST tubes, slowly inject the first standard solution over a period of 25 seconds. Wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.4 Inject a second standard (if required) over a period of 25 seconds and wait for 5 sec before withdrawing the syringe from the injector port.

7.7.1.5 Repeat the sequence above as required until all of the necessary compounds are spiked onto the VOST tubes.

7.7.1.6 Wait for 30 seconds, with gas flow, after the last spike before disconnecting the tubes. The total time the tubes are connected to the injector port with gas flow should not exceed 2.5 minutes. Total gas flow through the tubes during the spiking process should not exceed 25 mL to prevent break through of adsorbed compounds during the spiking process. To allow more time for connecting and disconnecting tubes, an on/off valve may be installed in the gas line to the injector port so that gas is not flowing through the tubes during the connection/disconnection process.

7.8 Prepare the purge-and-trap unit with 5 mL of organic-free reagent water in the purge vessel.

7.9 Connect the paired VOST tubes to the gas lines in the tube desorption unit. The tubes must be connected so that the gas flow during desorption will be opposite to the flow of gas during sampling: i.e., the tube desorption gas passes through the charcoal portion of the tube first. An on/off valve may be installed in the gas line leading to the tube desorption unit in order to prevent flow of gas through the tubes during the connection process.

7.10 Initiate tube desorption/purge and heating of the VOST tubes in the desorption apparatus.

7.11 Set the oven of the gas chromatograph to subambient temperatures by cooling with liquid nitrogen.

7.12 Prepare the GC/MS system for data acquisition.

7.13 At the conclusion of the tube/water purge time, attach the analytical trap to the gas chromatograph, adjust the purge-and-trap device to the desorb mode, and initiate the gas chromatographic program and the GC/MS data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the analytical trap to 180°C while backflushing the trap with inert gas at 2.5 mL/min for 5 min. Initiate the program for the gas chromatograph and simultaneously initiate data acquisition on the GC/MS system.

7.14 While the analytical trap is being desorbed into the gas chromatograph, empty the purging vessel. Wash the purging vessel with a minimum of two 5 mL flushes of organic-free reagent water (or methanol followed by organic-free reagent water) to avoid carryover of analytes into subsequent analyses.

7.15 After the sample has been desorbed, recondition the analytical trap by employing a bake cycle on the purge-and-trap unit. The analytical trap may be baked at temperatures up to 220°C. However, extensive use of high temperatures to recondition the trap will shorten the useful life of the analytical trap. After approximately 11 minutes, terminate the trap bake and cool the trap to ambient temperatures in preparation for the next sample. This procedure is a convention for reasonable samples and should be adequate if the concentration of contamination does not saturate the analytical system. If the organic compound concentration is so high that the analytical system is saturated beyond the point where even extended system bakeout is not sufficient to clean the system, a more extensive system maintenance must be performed. To perform extensive system maintenance, the analytical trap is replaced and the new trap is conditioned. Maintenance is performed on the GC column by removing at least one foot from the front end of the column. If the chromatography does not recover after column maintenance, the chromatographic column must be replaced. The ion source should be baked out and, if the bakeout is not sufficient to restore mass spectrometric peak shape and sensitivity, the ion source and the quadrupole rods must be cleaned.

7.16 Initial calibration for the analysis of VOST tubes: It is essential that calibration be performed in the mode in which analysis will be performed. If tubes are being analyzed as pairs, calibration standards should be prepared on paired tubes. If tubes are being analyzed individually, a calibration should be performed on individual Tenax® only tubes and Tenax®/charcoal tubes.

7.16.1 Prepare the calibration standards by spiking VOST tubes using the procedure described in Section 7.7.1. Spike each pair of VOST tubes (or each of the individual tubes) immediately before analysis. Perform the calibration analyses in order from low concentration to high to minimize the compound carryover. Add 5.0 mL of organic-free reagent water to the purging vessel. Initiate tube desorb/purge according to the procedure described above.

7.16.2 Tabulate the area response of the characteristic primary ions (Table 1) against concentration for each target compound, each surrogate compound, and each internal standard. The first criterion for quantitative analysis is correct identification of compounds. The compounds must elute within ± 0.06 retention time units of the elution time of the standard analyzed on the same analytical system on the day of

the analysis. The analytes should be quantitated relative to the closest eluting internal standard, according to the scheme shown in Table 4. Calculate response factors (RF) for each compound relative to the internal standard shown in Table 4. The internal standard selected for the calculation of RF is the internal standard that has a retention time closest to the compound being measured. The RF is calculated as follows:

$$RF = (A_x/C_{is})/(A_{is}/C_x)$$

where:

A_x = area of the characteristic ion for the compound being measured.

A_{is} = area of the characteristic ion for the specific internal standard.

C_{is} = concentration of the specific internal standard.

C_x = concentration of the compound being measured.

7.16.3 The average RF must be calculated for each compound. A system performance check should be made before the calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane, 1,1-dichloroethane, bromoform, 1,1,2,2-tetrachloroethane, and chlorobenzene. The minimum acceptable average RF for these compounds should be 0.300 (0.250 for bromoform). These compounds typically have RFs of 0.4 - 0.6, and are used to check compound instability and check for degradation caused by contaminated lines or active sites in the system. Examples of these occurrences are:

7.16.3.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.16.3.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in transfer lines may adversely affect response. Response of the primary quantitation ion (m/z 173) is directly affected by the tuning for 4-bromofluorobenzene at the ions of masses 174 and 176. Increasing the ratio of ions 174 and 176 to mass 95 (the base peak of the mass spectrum of bromofluorobenzene) may improve bromoform response.

7.16.3.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.16.4 Using the response factors from the initial calibration, calculate the percent relative standard deviation (%RSD) for the Calibration Check Compounds (CCCs).

$$\%RSD = (SD/\bar{X}) \times 100$$

where:

- %RSD = percent relative standard deviation
- RF_i = individual RF measurement
- \overline{RF} = mean of 5 initial RFs for a compound (the 5 points over the calibration range)
- SD = standard deviation of average RFs for a compound, where SD is calculated:

$$SD = \sqrt{\frac{\sum_{i=1}^N (RF_i - \overline{RF})^2}{N-1}}$$

The %RSD for each individual CCC should be less than 30 percent. This criterion must be met in order for the individual calibration to be valid. The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

7.17 Daily GC/MS Calibration

7.17.1 Prior to the analysis of samples, purge 50 ng of the 4-bromofluorobenzene standard. The resultant mass spectrum for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated every twelve hours of operation.

7.17.2 The initial calibration curve (Section 7.16) for each compound of interest must be checked and verified once every twelve hours of analysis time. This verification is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS and checking the SPCC (Section 7.16.3) and CCC (Section 7.16.4).

7.17.3 System Performance Check Compounds (SPCCs): A system performance check must be made each twelve hours of analysis. If the SPCC criteria are met, a comparison of response factors is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum response factors are not achieved, the system must be evaluated, and corrective action must be taken before analysis is allowed to begin. The minimum response factor for volatile SPCCs is 0.300 (0.250 for bromoform). If these minimum response factors are not achieved, some possible problems may be degradation of the standard mixture, contamination of the injector port, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. If the problem is active sites at the front end of the analytical column, column maintenance (removal of approximately 1 foot from the front end of the column) may remedy the problem.

7.17.4 Calibration Check Compounds: After the system performance check has been met, CCCs listed in Section 7.16.4 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{(RF_i - RF_c) \times 100}{RF_i}$$

where:

RF_i = average response factor from initial calibration

RF_c = response factor from current calibration check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. Benzene, toluene, and styrene will have problems with response factors if Tenax® decomposition occurs (either as a result of sampling exposure or temperature degradation), since these compounds are decomposition products of Tenax®. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion of percent difference less than 25% is not met for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If a source of the problem cannot be determined after corrective action is taken, a new five-point calibration curve MUST be generated. The criteria for the CCCs MUST be met before quantitative analysis can begin.

7.17.5 Internal standard responses and retention times in the check calibration standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. A factor which may influence the retention times of the internal standards on sample tubes is the level of overall organic compound loading on the VOST tubes. If the VOST tubes are very highly loaded with either a single compound or with multiple organic compounds, retention times for standards and compounds of interest will be affected. If the area for the primary ion of any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration check, the gas chromatograph and mass spectrometer should be inspected for malfunctions and corrections must be made, as appropriate. If the level of organic loading of samples is high, areas for the primary ions of both compounds of interest and standards will be adversely affected. Calibration check standards should not be subject to variation, since the concentrations of organic compounds on these samples are set to be within the linear range of the instrumentation. If instrument malfunction has occurred, analyses of samples performed under conditions of malfunction may be invalidated.

7.18 GC/MS Analysis of Samples

7.18.1 Set up the cartridge desorption unit, purge-and-trap unit, and GC/MS as described above.

7.18.2 BFB tuning criteria and daily GC/MS calibration check criteria must be met before analyzing samples.

7.18.3 Adjust the helium purge gas flow rate (through the cartridges and purge vessel) to approximately 40 mL/min. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. A flow rate which is too high reduces the recovery of chloromethane, and an insufficient gas flow rate reduces the recovery of bromoform.

7.18.4 The first analysis performed after the tuning check and the calibration or daily calibration check is a method blank. The method blank consists of clean VOST tubes (both Tenax® and Tenax®/charcoal) which are spiked with surrogate compounds and internal standards according to the procedure described in Section 7.7.1. The tubes which are used for the method blanks should be from the same batch of sorbent as the sorbent used for the field samples. After the tubes are cleaned and prepared for shipment to the field, sufficient pairs of tubes should be retained from the same batch in the laboratory to provide method blanks during the analysis.

7.18.5 The organic-free reagent water for the purge vessel for the analysis of each of the VOST samples should be supplied from the laboratory inventory which is maintained with constant bubbling of inert gas to avoid contamination.

7.18.6 If the analysis of a pair of VOST tubes has a concentration of analytes that exceeds the initial calibration range, no reanalysis of desorbed VOST tubes is possible. An additional calibration point can be added to bracket the higher concentration encountered in the samples so that the calibration database encompasses six or more points. Alternatively, the data may be flagged in the report as "extrapolated beyond the upper range of the calibration." The use of the secondary ions shown in Table 1 is permissible only in the case of interference with the primary quantitation ion. Use of secondary ions to calculate compound concentration in the case of saturation of the primary ion is not an acceptable procedure, since a negative bias of an unpredictable magnitude is introduced into the quantitative data when saturation of the mass spectrum of a compound is encountered. If high organic loadings, either of a single compound or of multiple compounds, are encountered, it is vital that a method blank be analyzed prior to the analysis of another sample to demonstrate that no compound carryover is occurring. If concentrations of organic compounds are sufficiently high that carryover problems are profound, extensive bakeout of the purge-and-trap unit will be required. Complete replacement of the contaminated analytical trap, with the associated requirement for conditioning the new trap, may also be required for VOST samples which show excessive concentrations of organic compounds. Other measures which might be required for decontamination of the analytical system include bakeout of the mass spectrometer,

replacement of the filament of the mass spectrometer, cleaning of the ion source of the mass spectrometer, and/or (depending on the nature of the contamination) maintenance of the chromatographic column or replacement of the chromatographic column, with the associated requirement for conditioning the new chromatographic column.

7.19 Data Interpretation

7.19.1 Qualitative analysis:

7.19.1.1 The qualitative identification of compounds determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds should be identified as present when the criteria below are met.

7.19.1.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound specific retention time will be accepted as meeting this criterion.

7.19.1.1.2 The RRT of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.19.1.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.19.1.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.19.1.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background

spectra is important. Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria can be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.19.1.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the type of analyses being conducted. Guidelines for making tentative identification are:

(1) Relative intensities of major ions in the reference spectrum (ions > 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within $\pm 20\%$. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

Computer generated library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Only after visual comparison of sample with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification.

7.19.2 Quantitative analysis:

7.19.2.1 When a compound has been identified, the quantitative analysis of that compound will be based on the integrated abundance from the extracted ion current profile of the primary characteristic ion for that compound (Table 1). In the event that there is interference with the primary ion so that quantitative measurements cannot be made, a secondary ion may be used.

NOTE: Use of a secondary ion to perform quantitative calculations in the event of the saturation of the primary ion is not an acceptable procedure because of the unpredictable extent of the negative bias which is introduced. Quantitative calculations are performed using the internal standard technique. The internal standard used to perform quantitative calculations shall be the internal standard nearest the retention time of a given analyte (see Table 4).

7.19.2.2 Calculate the amount of each identified analyte from the VOST tubes as follows:

$$\text{Amount (ng)} = (A_s C_{is}) / (A_{is} RF)$$

where:

A_s = area of the characteristic ion for the analyte to be measured.

A_{is} = area of the characteristic ion of the internal standard.

C_{is} = amount (ng) of the internal standard.

7.19.2.3 The choice of methods for evaluating data collected using the VOST methodology for incinerator trial burns is a regulatory decision. Various procedures are used to decide whether blank correction should be performed and how blank correction should be performed. Regulatory agencies to which VOST data are submitted also vary in their preferences for data which are or which are not blank corrected.

7.19.2.4 The total amount of the POHCs of interest collected on a pair of traps should be summed.

7.19.2.5 The occurrence of high concentrations of analytes on method blank cartridges indicates possible residual contamination of sorbent cartridges prior to shipment and use at the sampling site. Data with high associated blank values must be qualified with respect to validity, and all blank data should be reported separately. No blank corrections should be made in this case. Whether or not data of this type can be applied to the determination of Destruction and Removal Efficiency is a regulatory decision. Continued observation of high concentrations of analytes on blank sorbent cartridges indicates that procedures for cleanup and quality control for the sampling tubes are inadequate. Corrective action MUST be applied to tube preparation and monitoring procedures to maintain method blank concentrations below detection limits for analytes.

7.19.2.6 Where applicable, an estimate of concentration for noncalibrated components in the sample may be made. The formulae for quantitative calculations presented above should be used with the following modifications: The areas A_x and A_{is} should be from the

total ion chromatograms, and the Response Factor for the noncalibrated compound should be assumed to be 1. The nearest eluting internal standard free from interferences in the total ion chromatogram should be used to determine the concentration. The concentration which is obtained should be reported indicating: (1) that the value is an estimate; and (2) which internal standard was used.

7.19.2.7 If any internal standard recoveries fall outside the control limits established in Section 8.4, data for all analytes determined for that cartridge(s) must be qualified with the observation. Report results without correction for surrogate compound recovery data. When duplicates are analyzed, report the data obtained with the sample results.

8.0 QUALITY CONTROL

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

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank (laboratory blank sorbent tubes, reagent water purge) that interferences from the analytical system, glassware, sorbent tube preparation, and reagents are under control. Each time a new batch of sorbent tubes is analyzed, a method blank should be processed as a safeguard against chronic laboratory contamination. Blank tubes which have been carried through all the stages of sorbent preparation and handling should be used in the analysis.

8.3 The experience of the analyst performing the GC/MS analyses is invaluable to the success of the analytical methods. Each day that the analysis is performed, the daily calibration check standard should be evaluated to determine if the chromatographic and tube desorption systems are operating properly. Questions that should be asked are: Do the peaks look normal? Is the system response obtained comparable to the response from previous calibrations? Careful examination of the chromatogram of the calibration standard can indicate whether column maintenance is required or whether the column is still usable, whether there are leaks in the system, whether the injector septum requires replacing, etc. If changes are made to the system (such as change of a column), a calibration check must be carried out and a new multipoint calibration must be generated.

8.4 Required instrument quality control is found in the following sections:

8.4.1 The mass spectrometer must be tuned to meet the specifications for 4-bromofluorobenzene in Section 7.2 (Table 3).

8.4.2 An initial calibration of the tube desorption/purge-and-trap/GC/MS must be performed as specified in Section 7.7.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Section 7.16.3 and the CCC criteria in Section 7.16.4 each twelve hours of instrument operation.

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

8.5.1 A quality control (QC) check sample concentrate is required containing each analyte at a concentration of 10 mg/L in high purity methanol. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If the QC check sample concentrate is prepared by the laboratory, the QC check sample concentrate must be prepared using stock standards prepared independently from the stock standards used for calibration.

8.5.2 Spike four pairs of cleaned, prepared VOST tubes with 10 μ L of the QC check sample concentrate and analyze these spiked VOST tubes according to the method beginning in Section 7.0.

8.5.3 Calculate the average recovery (X) in ng and the standard deviation of the recovery (s) in ng for each analyte using the results of the four analyses.

8.5.4 The average recovery and standard deviation must fall within the expected range for determination of volatile organic compounds using the VOST analytical methodology. The expected range for recovery of volatile organic compounds using this method is 50-150%. Standard deviation will be compound dependent, but should, in general, range from 15 to 30 ng. More detailed method performance criteria must be generated from historical records in the laboratory or from interlaboratory studies coordinated by the Environmental Protection Agency. Since the additional steps of sorbent tube spiking and desorption are superimposed upon the methodology of Method 8240, direct transposition of Method 8240 criteria is questionable. If the recovery and standard deviation for all analytes meet the acceptance criteria, the system performance is acceptable and the analysis of field samples may begin. If any individual standard deviation exceeds the precision limit or any individual recovery falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes listed in Table 1 presents a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes for this method are determined.

8.5.5 When one or more of the analytes tested fails at least one of the acceptance criteria, the analyst must proceed according to one of the alternatives below.

8.5.5.1 Locate and correct the source of any problem with the methodology and repeat the test for all the analytes beginning with Section 8.5.2.

8.5.5.2 Beginning with Section 8.5.2, repeat the test only for those analytes that have failed to meet acceptance criteria. Repeated failure, however, will confirm a general problem either with the measurement system or with the applicability of the methodology to the particular analyte (especially if the analyte in question is not listed in Table 1). If the problem is identified as originating in the measurement system, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.5.2.

8.6 To determine acceptable accuracy and precision limits for surrogate standards, the following procedure should be performed.

8.6.1 For each sample analyzed, calculate the percent recovery of each surrogate compound in the sample.

8.6.2 Once a minimum of thirty samples has been analyzed, calculate the average percent recovery (p) and the standard deviation of the percent recovery (s) for each of the surrogate compounds.

8.6.3 Calculate the upper and lower control limits for method performance for each surrogate standard. This calculation is performed as follows:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= p + 3s \\ \text{Lower Control Limit (LCL)} &= p - 3s\end{aligned}$$

For reference, the comparable control limits for recovery of the surrogate compounds from water and soil in Method 8240 are:

4-Bromofluorobenzene	Water: 86-115%	Soil: 74-121%
1,2-Dichloroethane- d_4	Water: 76-114%	Soil: 70-121%
Toluene- d_8	Water: 88-110%	Soil: 81-117%

The control limits for the VOST methodology would be expected to be similar, but exact data are not presently available. Individual laboratory control limits can be established by the analysis of replicate samples.

8.6.4 If surrogate recovery is not within the limits established by the laboratory, the following procedures are required: (1) Verify that there are no errors in calculations, preparation of surrogate spiking solutions, and preparation of internal standard spiking solutions. Also, verify that instrument performance criteria have been met. (2) Recalculate the data and/or analyze a replicate sample, if replicates are available.

(3) If all instrument performance criteria are met and recovery of surrogates from spiked blank VOST tubes (analysis of a method blank) is acceptable, the problem is due to the matrix. Emissions samples may be highly acidic and may be highly loaded with target and non target organic compounds. Both of these conditions will affect the ability to recover surrogate compounds which are spiked on the field samples. The surrogate compound recovery is thus a valuable indicator of the interactions of sampled compounds with the matrix. If surrogates spiked immediately before analysis cannot be observed with acceptable recovery, the implications for target organic analytes which have been sampled in the field must be assessed very carefully. If chemical or other interactions are occurring on the exposed tubes, the failure to observe an analyte may not necessarily imply that the Destruction and Removal Efficiency for that analyte is high.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples analyzed. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer may be used, if replicate samples showing the same compound are available. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined in Chapter One. The MDL concentrations listed in Table 2 were obtained using cleaned blanked VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under these conditions, the method detection limit for spiked compounds in extremely complex matrices may be larger by a factor of 500-1000.

10.0 REFERENCES

1. Protocol for Collection and Analysis of Volatile POHCs Using VOST. EPA/600/8-84-007, March, 1984.
2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014A, January, 1986.
3. U. S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act, Method 624," October 26, 1984.
4. Bellar, T. A., and J. J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), 739-744, 1974.

5. Bellar, T. A., and J. J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp 108-129, 1979.

TABLE 1.
RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS
WHICH CAN BE ANALYZED BY METHOD 5041

Compound	Retention Time (min)	Primary Ion Mass	Secondary Ion(s) Mass(es)
Acetone	7.1	43	58
Acrylonitrile	8.6	53	52, 51
Benzene	13.3	78	52, 77
Bromochloromethane	12.0	128	49, 130, 51
Bromodichloromethane	16.0	83	85, 129
4-Bromofluorobenzene	23.4	95	174, 176
Bromoform	22.5	173	171, 175, 252
Bromomethane	4.1	94	96, 79
Carbon disulfide	7.1	76	78
Carbon tetrachloride	12.6	117	119, 121
Chlorobenzene	20.5	112	114, 77
Chlorodibromomethane	19.3	129	208, 206
Chloroethane	4.2	64	66, 49
Chloroform	12.2	83	85, 47
Chloromethane	3.0	50	52, 49
Dibromomethane	15.4	93	174, 95
1,1-Dichloroethane	10.0	63	65, 83
1,2-Dichloroethane	13.3	62	64, 98
1,1-Dichloroethene	6.4	96	61, 98
trans-1,2-Dichloroethene	8.6	96	61, 98
1,2-Dichloropropane	15.2	63	62, 41
cis-1,3-Dichloropropene	17.0	75	77, 39
trans-1,3-Dichloropropene	18.2	75	77, 39
1,4-Difluorobenzene	14.2	114	63, 88
Ethylbenzene	21.1	106	91
Iodomethane	7.0	142	127, 141
Methylene chloride	8.1	84	49, 51, 86
Styrene	22.3	104	78, 103
1,1,2,2-Tetrachloroethane	24.0	83	85, 131, 133
Tetrachloroethene	18.6	164	129, 131, 166
Toluene	17.4	92	91, 65
1,1,1-Trichloroethane	12.4	97	99, 117
1,1,2-Trichloroethane	18.4	97	83, 85, 99
Trichloroethene	14.5	130	95, 97, 132
Trichlorofluoromethane	5.1	101	103, 66
1,2,3-Trichloropropane	24.0	75	110, 77, 61
Vinyl chloride	3.2	62	64, 61
Xylenes*	22.2	106	91

* The retention time given is for m- and p-xylene, which coelute on the Megabor column. o-Xylene elutes approximately 50 seconds later.

TABLE 2.
PRELIMINARY METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS ANALYZED BY METHOD 5041*

Compound	CAS Number	Detection Limit, ng	Boiling Point, °C
Chloromethane	74-87-3	58	-24
Bromomethane	74-83-9	26	4
Vinyl chloride	75-01-4	14	-13
Chloroethane	75-00-3	21	13
Methylene chloride	75-09-2	9	40
Acetone	67-64-1	35	56
Carbon disulfide	75-15-0	11	46
1,1-Dichloroethene	75-35-4	14	32
1,1-Dichloroethane	75-35-3	12	57
trans-1,2-Dichloroethene	156-60-5	11	48
Chloroform	67-66-3	11	62
1,2-Dichloroethane	107-06-2	13	83
1,1,1-Trichloroethane	71-55-6	8	74
Carbon tetrachloride	56-23-5	8	77
Bromodichloromethane	75-27-4	11	88
1,1,2,2-Tetrachloroethane**	79-34-5	23	146
1,2-Dichloropropane	78-87-5	12	95
trans-1,3-Dichloropropene	10061-02-6	17	112
Trichloroethene	79-01-6	11	87
Dibromochloromethane	124-48-1	21	122
1,1,2-Trichloroethane	79-00-5	26	114
Benzene	71-43-2	26	80
cis-1,3-Dichloropropene	10061-01-5	27	112
Bromoform**	75-25-2	26	150
Tetrachloroethene	127-18-4	11	121
Toluene	108-88-3	15	111
Chlorobenzene**	108-90-7	15	132
Ethylbenzene**	100-41-4	21	136
Styrene	100-42-5	46	145
Trichlorofluoromethane	75-69-4	17	24
Iodomethane	74-88-4	9	43
Acrylonitrile	107-13-1	13	78
Dibromomethane	74-95-3	14	97
1,2,3-Trichloropropane**	96-18-4	37	157
total Xylenes		22	138-144

* The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. The detection limits cited above were determined according to Title 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Not appropriate for quantitative sampling by Method 0030.

TABLE 3.
KEY ION ABUNDANCE CRITERIA FOR 4-BROMOFLUOROBENZENE

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95%, but less than 101% of mass 174
177	5 to 9% of mass 176

TABLE 4.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

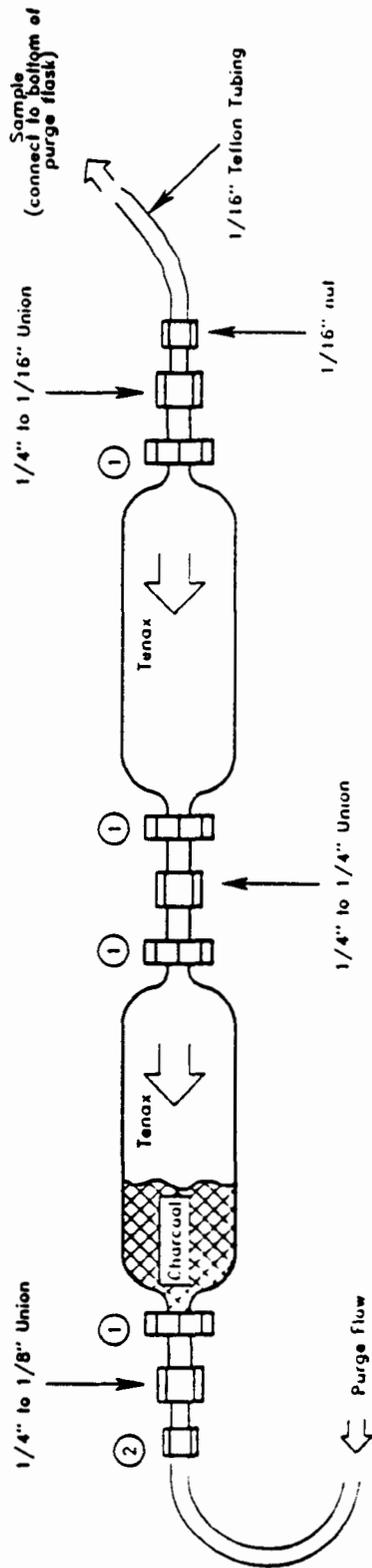
Bromochloromethane

Acetone
Acrylonitrile
Bromomethane
Carbon disulfide
Chloroethane
Chloroform
Chloromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,2-Dichloroethane-d₄ (surrogate)
1,1-Dichloroethene
Trichloroethene
trans-1,2-Dichloroethene
Iodomethane
Methylene chloride
Trichlorofluoromethane
Vinyl chloride

1,4-Difluorobenzene

Benzene
Bromodichloromethane
Bromoform
Carbon tetrachloride
Chlorodibromomethane
Dibromomethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,1,1-Trichloroethane
1,1,2-Trichloroethane

Chlorobenzene-d₅
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d₈ (surrogate)
1,2,3-Trichloropropane
Xylenes



- | | |
|---|----------|
| ① | 1/4" nut |
| ② | 1/8" nut |

Figure 1. Cartridge Desorption Flow

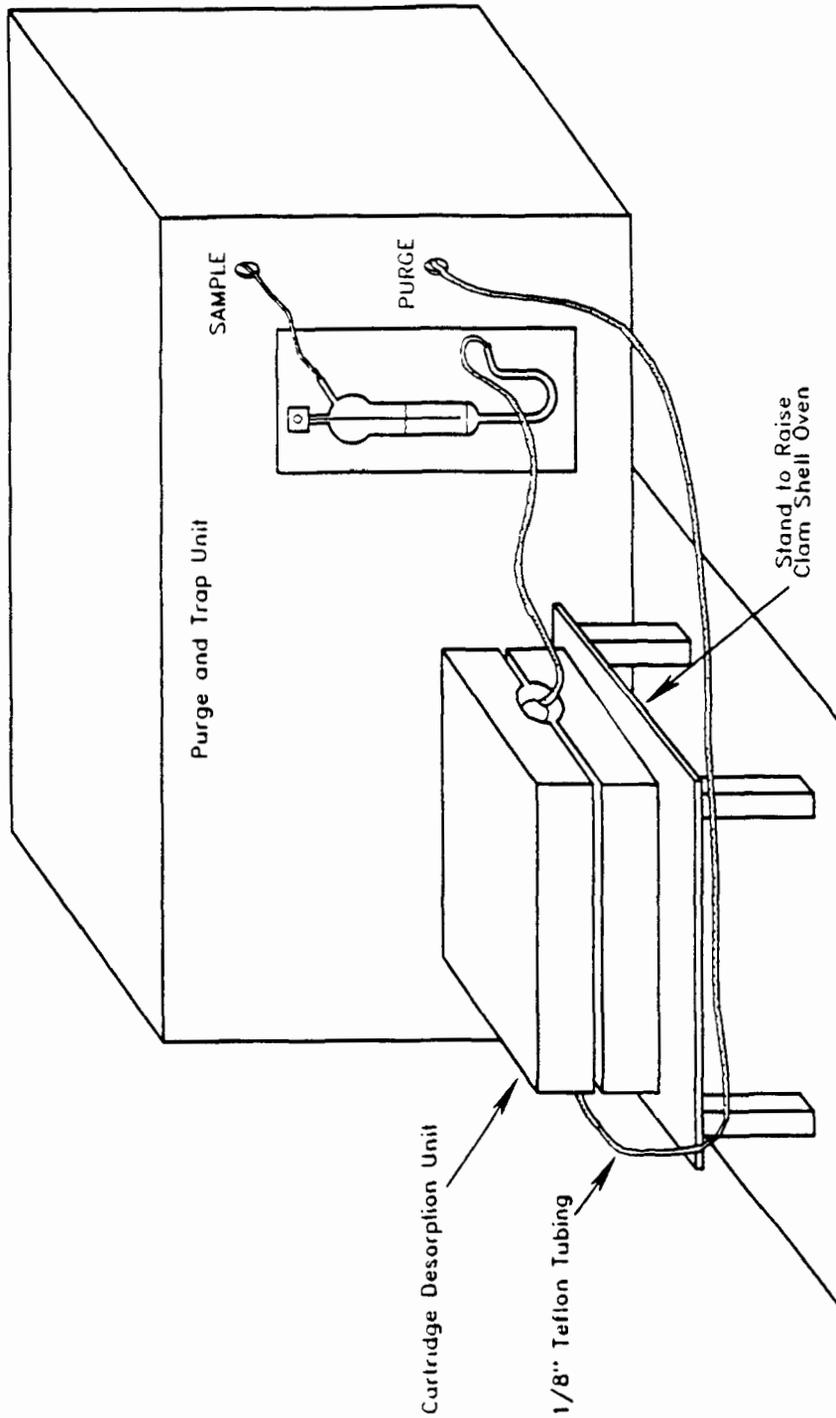


Figure 2. Cartridge Desorption Unit with Purge and Trap Unit

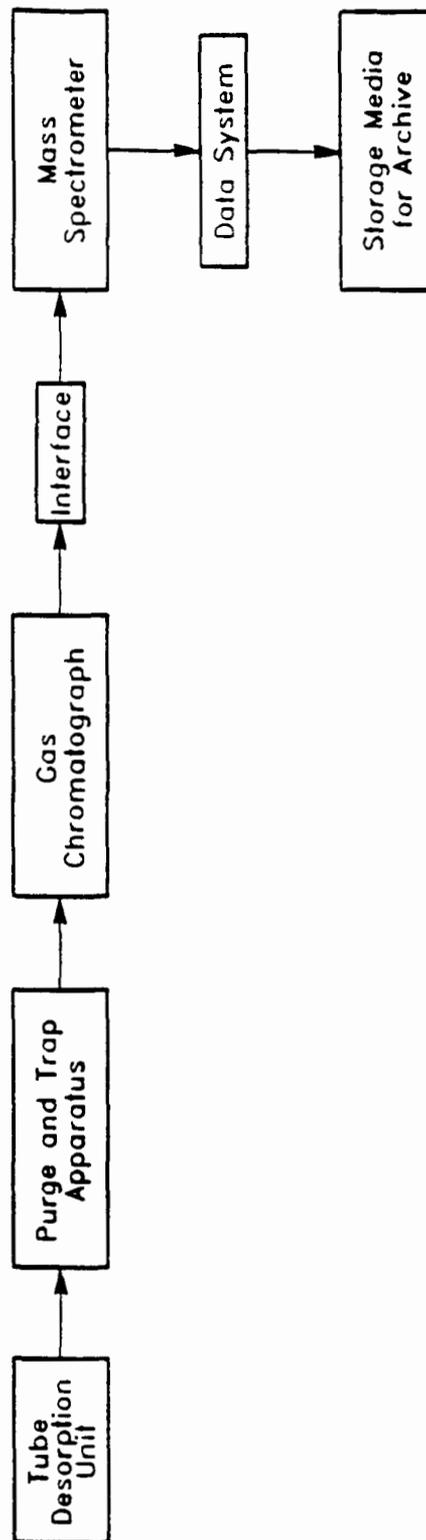


Figure 3. Schematic Diagram of Overall Analytical System

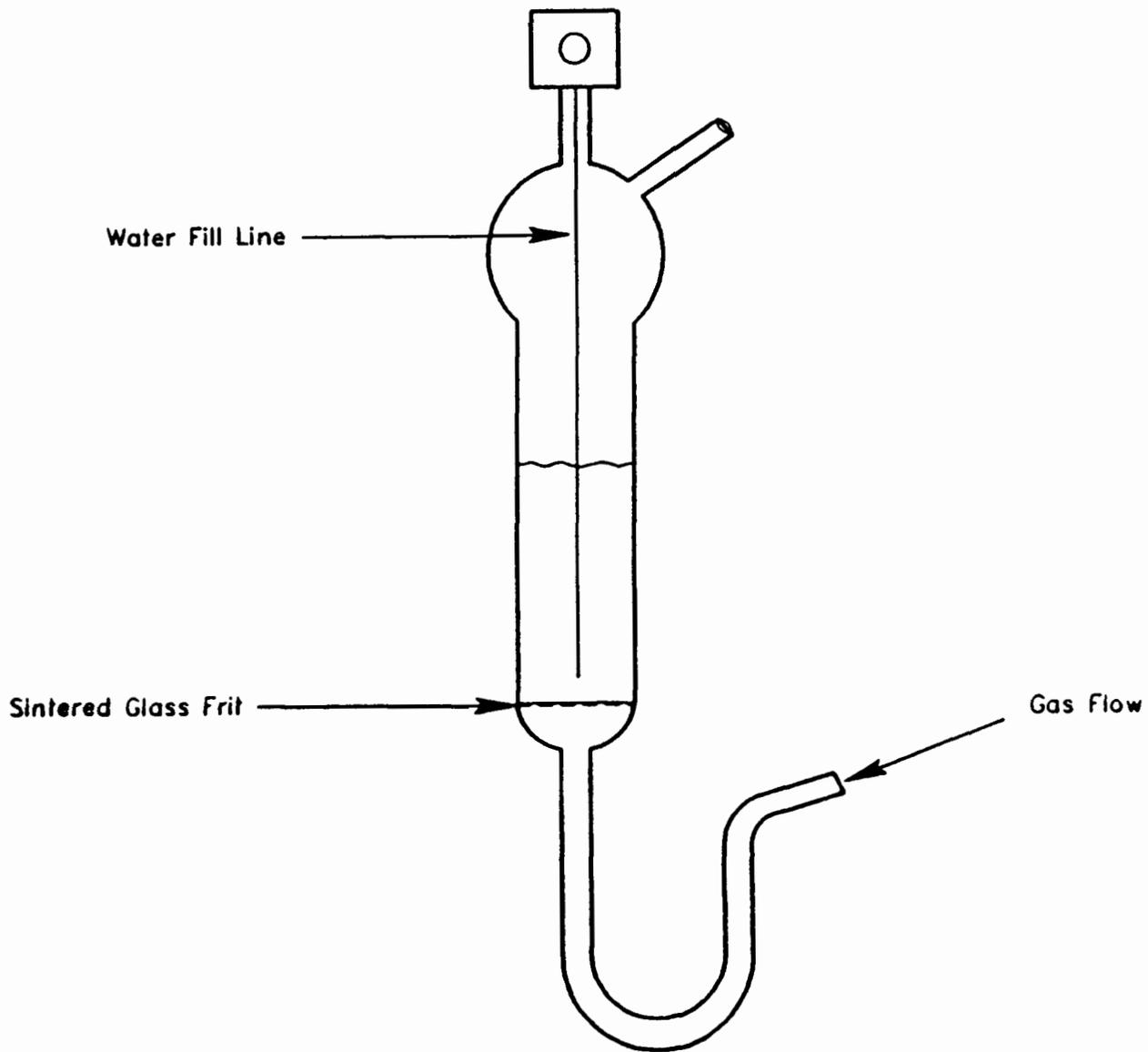


Figure 4. Sample Purge Vessel

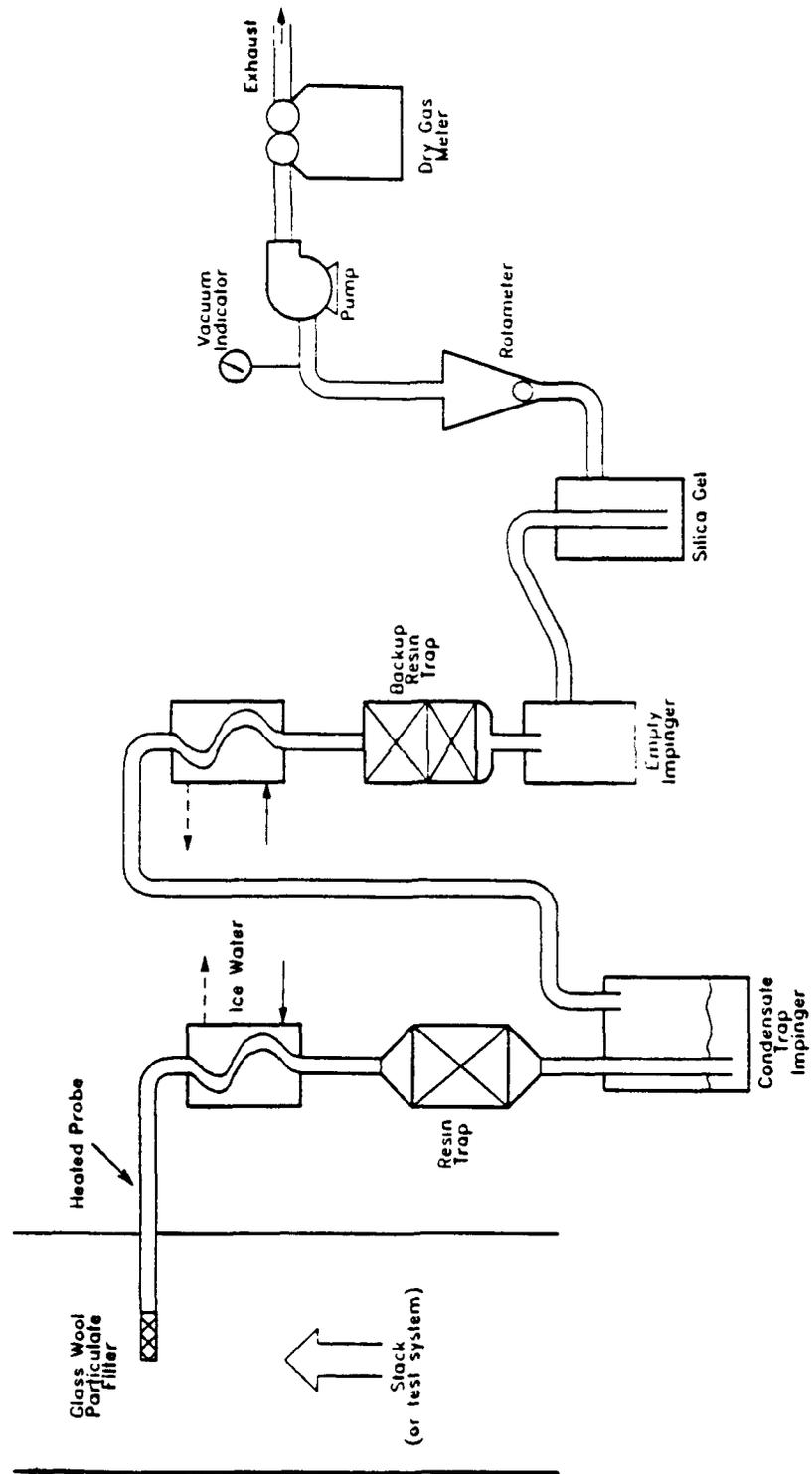
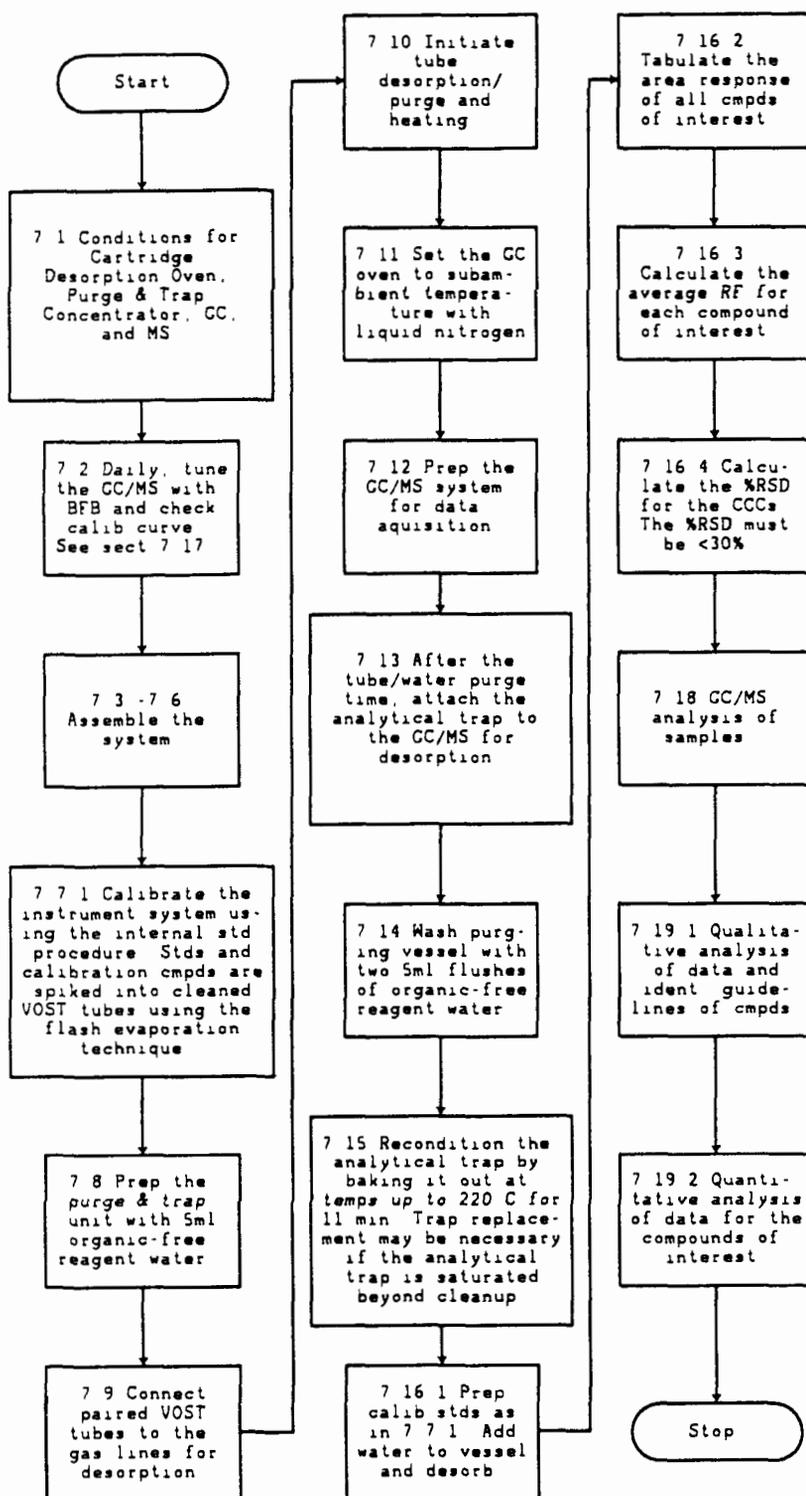


Figure 5. Schematic of Volatile Organic Sampling Train (VOST)

METHOD 5041
 PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC
 SAMPLING TRAIN: WIDE-BORE CAPILLARY COLUMN TECHNIQUE



METHOD 5100

DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the volatile organic concentration of hazardous wastes.

1.2 Performance of this method should not be attempted by persons unfamiliar with the operation of a flame ionization detector (FID) or a Hall electrolytic conductivity detector (HECD), because knowledge beyond the scope of this presentation is required.

2.0 SUMMARY OF METHOD

2.1 A sample of waste is collected from a source as close to the point of generation as practical. The sample is then heated and purged with nitrogen to separate the volatile organic compounds. Part of the sample is analyzed for carbon concentration, as methane, with an FID, and part of the sample is analyzed for chlorine concentration, as chloride, with an HECD. The volatile organic concentration is the sum of the measured carbon and chlorine concentrations of the sample.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

4.0 APPARATUS AND MATERIALS

4.1 Sampling. The following equipment is required:

4.1.1 Static Mixer. Installed in-line or as a by-pass loop, sized so that the drop size of the dispersed phase is no greater than 1,000 μm . If the installation of the mixer is in a by-pass loop, then the entire waste stream must be diverted through the mixer.

4.1.2 Tap. Installed no further than two pipe diameters downstream of the static mixer outlet.

4.1.3 Sampling Tube. Flexible Teflon, 0.25 in. ID.

4.1.4 Sample Container. Borosilicate glass or Teflon, 15 to 50 mL, and a Teflon lined screw cap capable of forming an air tight seal.

4.1.5 Cooling Coil. Fabricated from 0.25 in. ID 304 stainless steel tubing with a thermocouple at the coil outlet.

4.2 Analysis. The following equipment is required:

4.2.1 Purging Apparatus. For separating the volatile organics from the waste sample. A schematic of the system is shown in Figure 1. The purging apparatus consists of the following major components:

4.2.1.1 Purging Chamber. A glass container to hold the sample while it is heated and purged with dry nitrogen. Exact dimensions are shown in Figure 3.

The cap of the purging chamber is equipped with three fittings: one for a mechanical stirrer (fitted with the #11 Ace thread), one for a thermometer (top fitting), and one for the Teflon exit tubing (side fitting) as shown in Figure 3.

The base of the purging chamber is a 50 mm inside diameter (ID) cylindrical glass tube. One end of the tube is fitted with a 50 mm Ace-thread fitting, while the other end is sealed. Near the sealed end in the side wall is a fitting for a glass purging lance.

4.2.1.2 Purging Lance. Glass tube, 6 mm ID by 15.25 cm long, bent into an "L" shape. The "L" end of the tube is sealed, and then pierced with fifteen holes, each 1 mm in diameter.

4.2.1.3 Mechanical Stirrer. Stainless steel or Teflon stirring rod driven by an electric motor.

4.2.1.4 Coalescing Filter. Porous fritted disc incorporated into a container with the same dimensions as the purging chamber. The details of the design are shown in Figure 3.

4.2.1.5 Constant Temperature Bath. Capable of maintaining a temperature around the purging chamber and coalescing filter of $75 \pm 5^\circ\text{C}$.

4.2.1.6 Three-way Valves. Two, manually operated, stainless steel.

4.2.1.7 Flow Controller. Capable of maintaining a purge gas flow rate of 6 ± 0.006 L/min.

4.2.1.8 Rotameters. Two for monitoring the air flow through the purging system (0-20 L/min).

4.2.1.9 Sample Splitters. Two heated flow restrictors. At a purge rate of up to 6 L/min, one will supply a constant flow of 70 to 100 mL/min to the analyzers. The second will split the analytical flow between the FID and the HECD. The approximate flow to the FID will be 40 mL/min and to the HECD will be 15 mL/min, but the exact flow must be adjusted to be compatible with the individual detector and to meet its linearity requirement.

4.2.1.10 Adsorbent Tube. To hold 10 g of activated charcoal. Excess purge gas is vented through the adsorbent tube to prevent any potentially hazardous materials from entering the laboratory.

4.2.2 Volatile Organic Measurement System. Consisting of an FID to measure the carbon concentration of the sample, and an HECD to measure the chlorine concentration (as chloride).

4.2.2.1 FID. An FID meeting the following specifications is required:

4.2.2.1.1 Linearity. A linear response (± 5 percent) over the operating range as demonstrated by the procedures established in Section 8.1.1.

4.2.2.1.2 Range. A full scale range of 50 pg carbon/sec to 50 μ g carbon/sec. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

4.2.2.1.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

4.2.2.2 HECD. An HECD meeting the following specifications is required:

4.2.2.2.1 Linearity. A linear response (± 10 percent) over the response range as demonstrated by the procedures in Section 8.1.2.

4.2.2.2.2 Range. A full scale range of 5.0 pg/sec to 500 ng/sec chloride. Signal attenuators shall be available to produce a minimum signal response of 10 percent of full scale.

4.2.2.2.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the output voltage range of HECD.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without adversely impacting the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

5.3 Sampling.

5.3.1 Polyethylene glycol (PEG), 98 percent pure with an average molecular weight of 400. Remove any organic compounds that may be detected as volatile organics already present in the polyethylene glycol before it is used, by heating it to 250°C and purging it with nitrogen at a flow rate of 1 to 2 L/min for 2 hours. Waste PEG must be disposed of properly (consult local, State and Federal guidelines and regulations).

5.4 Analysis.

5.4.1 Sample Separation. The following are required for the sample purging step:

5.4.1.1 Polyethylene glycol. Same as Section 5.3.1.

5.4.1.2 Silicone, Mineral, or Peanut Oil. For use as the heat dispersing medium in the constant temperature bath.

5.4.1.3 Purging Gas. Zero grade nitrogen (N₂), containing less than 1 ppm carbon.

5.4.2 Volatile Organics Measurement. The following are required for measuring the volatile organic concentrations:

5.4.2.1 Hydrogen (H₂). Zero grade H₂, 99.999 percent pure.

5.4.2.2 Combustion Gas. Zero grade air or oxygen, as required by the FID.

5.4.2.3 FID Calibration Gases.

5.4.2.3.1 Low-level Calibration Gas. Gas mixture standard with a nominal concentration of 35 ppm (v/v) propane in N₂.

5.4.2.3.2 Mid-level Calibration Gas. Gas mixture standard with a nominal concentration of 175 ppm (v/v) propane in N₂.

5.4.2.3.3 High-level Calibration Gas. Gas mixture standard with a nominal concentration of 350 ppm (v/v) propane in N₂.

5.4.2.4 HECD Calibration Gases.

5.4.2.4.1 Low-level Calibration Gas. Gas mixture standard with a nominal concentration of 20 ppm (v/v) 1,1-dichloroethene in N₂.

5.4.2.4.2 Mid-level Calibration Gas. Gas mixture standard with a nominal concentration of 100 ppm (v/v) 1,1-dichloroethene in N₂.

5.4.2.4.3 High-level Calibration Gas. Gas mixture standard with a nominal concentration of 200 ppm (v/v) 1,1-dichloroethene in N₂.

5.4.2.5 n-Propanol, CH₃CH₂CH₂OH. ACS grade or better.

5.4.2.6 Electrolyte Solution. For use in the conductivity detector. Mix together 500 mL of water and 500 mL of n-propanol and store in a glass container.

5.4.2.7 Charcoal. Activated coconut, 12 to 30 mesh.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Volume One, Section B, Chapter Four, "Organic Analytes," Section 4.1.

6.2 Sampling Plan Design and Development. Use the procedures given in Volume Two, Part III, Chapter Nine, "Sampling Plan."

6.3 Waste in Enclosed Pipes. Sample as close as practical to the point of waste generation in order to minimize the loss of organics. Assemble the sampling apparatus as shown in Figure 4. Install the static mixer in the process line or in a by-pass line. Locate the tap within two pipe diameters of the static mixer outlet.

6.4 Prepare the sampling containers as follows: Pour into the container an amount of PEG equal to the total volume of the sample container, less 10 mL. PEG will reduce, but not eliminate, the loss of volatile organic compounds during sample collection. Weigh the sample container with the screw cap, the PEG and any labels to the nearest 0.01 g, and record the weight (m_{st}). Before sampling, store the containers in an ice bath until the temperature of the PEG is less than 4°C.

6.5 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.

6.6 After purging, stop the sample flow and direct the sampling tube to a preweighed sample container, prepared as described in Section 6.4. Keep the tip of the tube below the surface of the PEG during sampling to minimize contact with the atmosphere. Sample at a flow rate such that the temperature of the waste is less than 10°C. Fill the sample container and immediately cap it (within 5 seconds) so that a minimum headspace exists in the container. Store immediately in a cooler and cover with ice.

6.7 Alternative sampling techniques may be used upon the approval of the Administrator.

7.0 PROCEDURE

7.1 Sample Recovery. Remove the sample container from the cooler, and wipe the exterior of the container to remove any extraneous ice, water, or other debris. Reweigh the sample container and sample to the nearest 0.01 g, and record the weight (m_{sf}). Pour the contents of the sample container into the purging flask. Rinse the sample container three times with PEG, transferring the rinsings to the purging flask after each rinse. The total volume of PEG in the purging flask shall be approximately 50 mL. Add approximately 50 mL of water.

7.2 Apparatus Assembly. Assemble the purging apparatus as shown in Figure 2, leaving the purging chamber out of the constant temperature bath. Adjust the stirring rod so that it nearly reaches the bottom of the chamber. Position the sparger so that it is within 1 cm of the bottom, but does not interfere with the stirring rod. Lower the thermometer so that it extends into the liquid.

7.3 Sample Analysis. Turn on the constant temperature bath and allow the temperature to equilibrate at $75 \pm 5^\circ\text{C}$. Turn the bypass valve so that the purge gas bypasses the purging chamber. Turn on the purge gas. Allow both the FID and the HECD to warm up until a stable baseline is achieved on each detector. Pack the adsorbent tube with 10 g of charcoal. Replace the charcoal after each run and dispose of the spent charcoal properly. Place the assembled chamber in the constant temperature bath. When the temperature of the PEG reaches $75 \pm 5^\circ\text{C}$, turn the bypass valve so that the purge gas flows through the purging chamber. Begin recording the response of the FID and the HECD. Compare the readings between the two rotameters in the system. If the readings differ by more than five percent, stop the purging and determine the source of the discrepancy before resuming.

As purging continues, monitor the output of the FID to make certain that the separation is proceeding correctly, and that the results are being properly recorded. Every 10 minutes, read and record the purge flow rate and the liquid temperature. Continue purging for 30 minutes.

7.4 Initial Performance Check of Purging System. Before placing the system in operation, after a shutdown of greater than six months, and after any major modification, conduct the linearity checks described in Sections 7.4.1 and 7.4.2. Install all calibration gases at the three-way calibration gas valve. See Figure 1.

7.4.1 FID Linearity Check and Calibration. With the purging system operating as in Section 7.3, allow the FID to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder, and inject the calibration gas by turning the calibration gas valve to switch flow from the purge gas to the calibration gas. Continue the calibration gas flow for approximately two minutes before switching to the purge gas. Make triplicate injections of each calibration gas (Section 5.4.2.3), and then calculate the average response factor for each concentration (R_i), as well as the overall mean of the response factor values, R_o . The instrument linearity is acceptable if each R_i is within 5 percent of R_o and if the relative standard deviation (Section 7.7.10) for each set of triplicate

injections is less than 5 percent. Record the overall mean value of the propane response factor values as the FID calibration response factor, R_o .

7.4.2 HECD Linearity Check and Calibration. With the purging system operating as in Section 7.3, allow the HECD to establish a stable baseline. Set the secondary pressure regulator of the calibration gas cylinder to the same pressure as the purge gas cylinder, and inject the calibration gas by turning the calibration gas valve to switch flow from the purge gas to the calibration gas. Continue the calibration gas flow for about two minutes before switching to the purge gas. Make triplicate injections of each calibration gas (Section 5.4.2.4), and then calculate the average response factor for each concentration, R_{th} , as well as the overall mean of the response factors, R_{oh} . The instrument linearity is acceptable if each R_{th} (Section 7.7.5) is within 10 percent of R_{oh} and if the relative standard deviation (Section 7.7.10) for each set of triplicate injections is less than 10 percent. Record the overall mean value of the chlorine response factors as the HECD response factor, R_{oh} .

7.5 Daily Calibrations.

7.5.1 FID Daily Calibration. Inject duplicate samples from the mid-level FID calibration gas (Section 5.4.2.3.2) as described in Section 7.4.1, and calculate the average daily response factor (DR_t). System operation is adequate if the DR_t is within 5 percent of the R_o calculated during the initial performance test (Section 7.4.1). Use the DR_t for calculation of carbon content in the samples.

7.5.2 HECD Daily Calibration. Inject duplicate samples from the mid-level HECD calibration gas (Section 5.4.2.4.2) as described in Section 7.4.2, and calculate the average daily response factor DR_{th} . The system operation is adequate if the DR_{th} is within 10 percent of the R_{oh} calculated during the initial performance test (Section 7.4.2). Use the DR_{th} for calculation of chlorine in the samples.

7.6 Water Blank. Transfer about 60 mL of organic-free reagent water into the purging chamber. Add 50 mL of PEG to the purging chamber. Treat the blank as described in Sections 7.2 and 7.3.

7.7 Calculations

7.7.1 Nomenclature.

A_b	=	Area under the water blank response curve, counts.
A_s	=	Area under the sample response curve, counts.
C	=	Concentration of volatile organic in the sample, ppm(w/w).
C_c	=	Concentration of FID calibration gas, ppm(v/v).
C_h	=	Concentration of HECD calibration gas, ppm(v/v).
DR_t	=	Average daily response factor of the FID, $\mu\text{g C}/\text{counts}$.

- DR_{th} = Average daily response factor of the HECD detector, $\mu\text{g Cl}^-/\text{counts}$.
 m_{co} = Mass of carbon, as methane, in the FID calibration standard, μg .
 m_{ch} = Mass of chloride in the HECD calibration standard, μg .
 m_s = Mass of the waste sample, g.
 m_{sc} = Mass of carbon, as methane, in the sample, μg .
 m_{sf} = Mass of sample container and waste sample, g.
 m_{sh} = Mass of chloride in the sample, μg .
 m_{st} = Mass of sample container prior to sampling, g.
 m_{vo} = Mass of volatile organic in the sample, μg .
 P_a = Ambient barometric pressure in the laboratory, Torr.
 Q_c = Flowrate of calibration gas, L/min.
 t_c = Length of time standard gas is delivered to the analyzer, min.
 T_a = Ambient temperature in the laboratory, $^{\circ}\text{K}$.

7.7.2 Mass of Carbon, as Methane in the FID Calibration Gas.

$$m_{co} = k_2 C_c t_c Q_c (P_a/T_a) \quad \text{Eq. 1}$$

where $k_2 = 0.5773 \mu\text{g C-}^{\circ}\text{K}/\mu\text{l-Torr}$

7.7.3 Mass of Chloride in the HECD Detector Calibration Gas.

$$m_{ch} = k_3 C_h t_c Q_c (P_a/T_a) \quad \text{Eq. 2}$$

where $k_3 = 1.1371 \mu\text{g Cl-}^{\circ}\text{K}/\mu\text{l-Torr}$

7.7.4 FID Response Factor.

$$R_t = m_{co}/A \quad \text{Eq. 3}$$

7.7.5 HECD Response Factor.

$$R_{th} = m_{ch}/A \quad \text{Eq. 4}$$

7.7.6 Mass of Carbon in the Sample.

$$m_{sc} = DR_t (A_s - A_b) \quad \text{Eq. 5}$$

7.7.7 Mass of Chloride in the Sample.

$$m_{sh} = DR_{th} (A_s - A_b) \quad \text{Eq. 6}$$

7.7.8 Mass of Volatile Organic in the Sample.

$$m = m_{sc} + m_{sh} \quad \text{Eq. 7}$$

7.7.9 Standard Deviation.

$$SD = 100x \left[\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{(n-1)} \right]^{1/2} \quad \text{Eq. 8}$$

7.7.10 Relative Standard Deviation.

$$RSD = SD/\bar{x} \quad \text{Eq. 9}$$

7.7.11 Mass of Sample.

$$m_s = m_{sf} - m_{st} \quad \text{Eq. 10}$$

7.7.12 Concentration of Volatile Organic in Waste.

$$C = m_{vo}/m_s \quad \text{Eq. 11}$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 Maintain a record of performance of all system checks and calibrations.

8.3 Calibrate analytical balance against standard weights.

9.0 METHOD PERFORMANCE

9.1 Performance data are not currently available.

10.0 REFERENCES

1. "Determination of the Volatile Organic Content of Waste Samples" Method 25D; Proposed Amendment to 40 CFR Part 60, Appendix A, January 1989.

FIGURE 1
Purging Apparatus

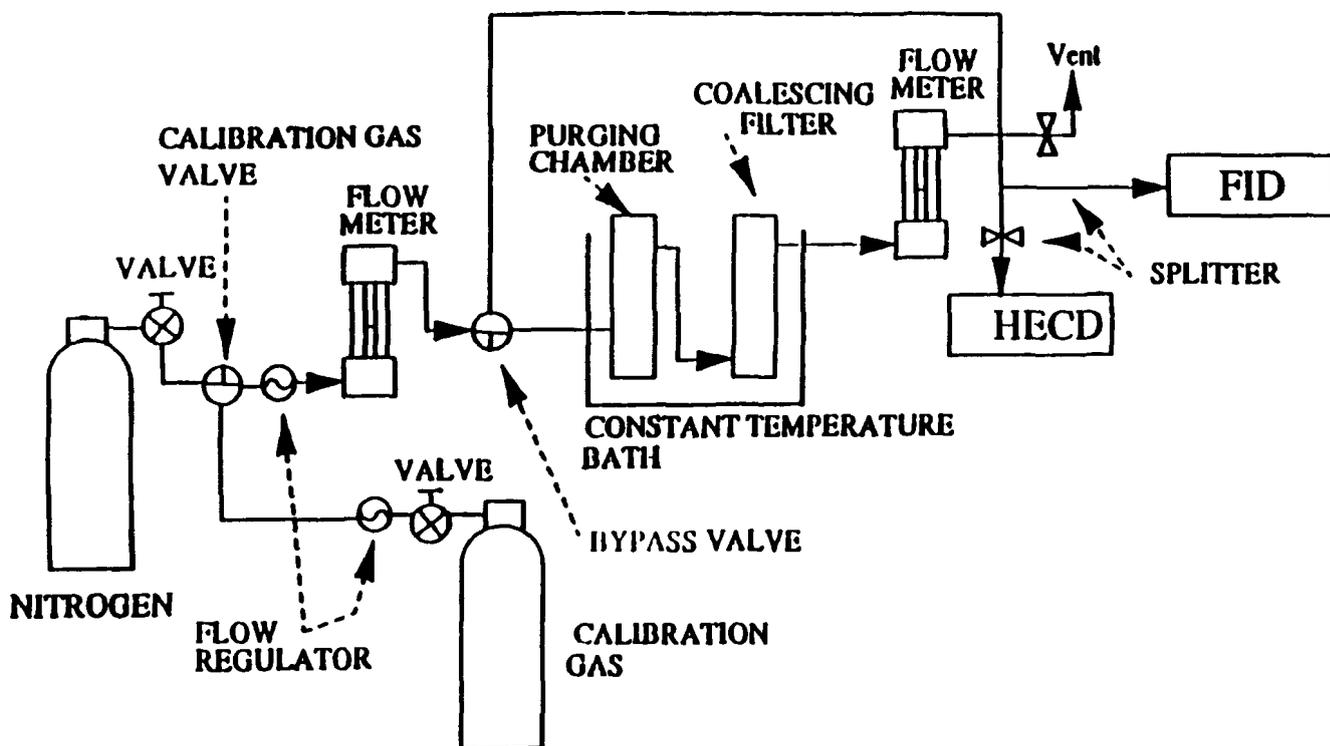


FIGURE 2

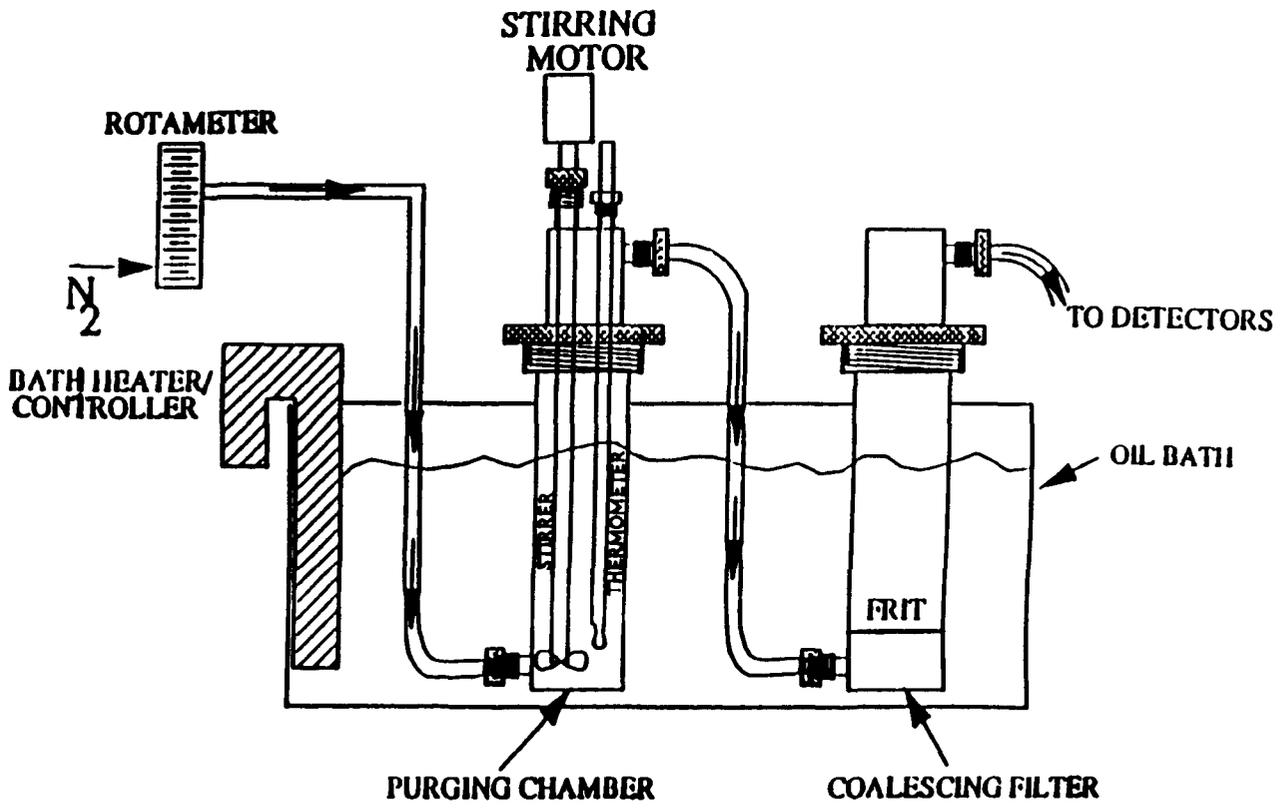


FIGURE 3
Purging Chamber

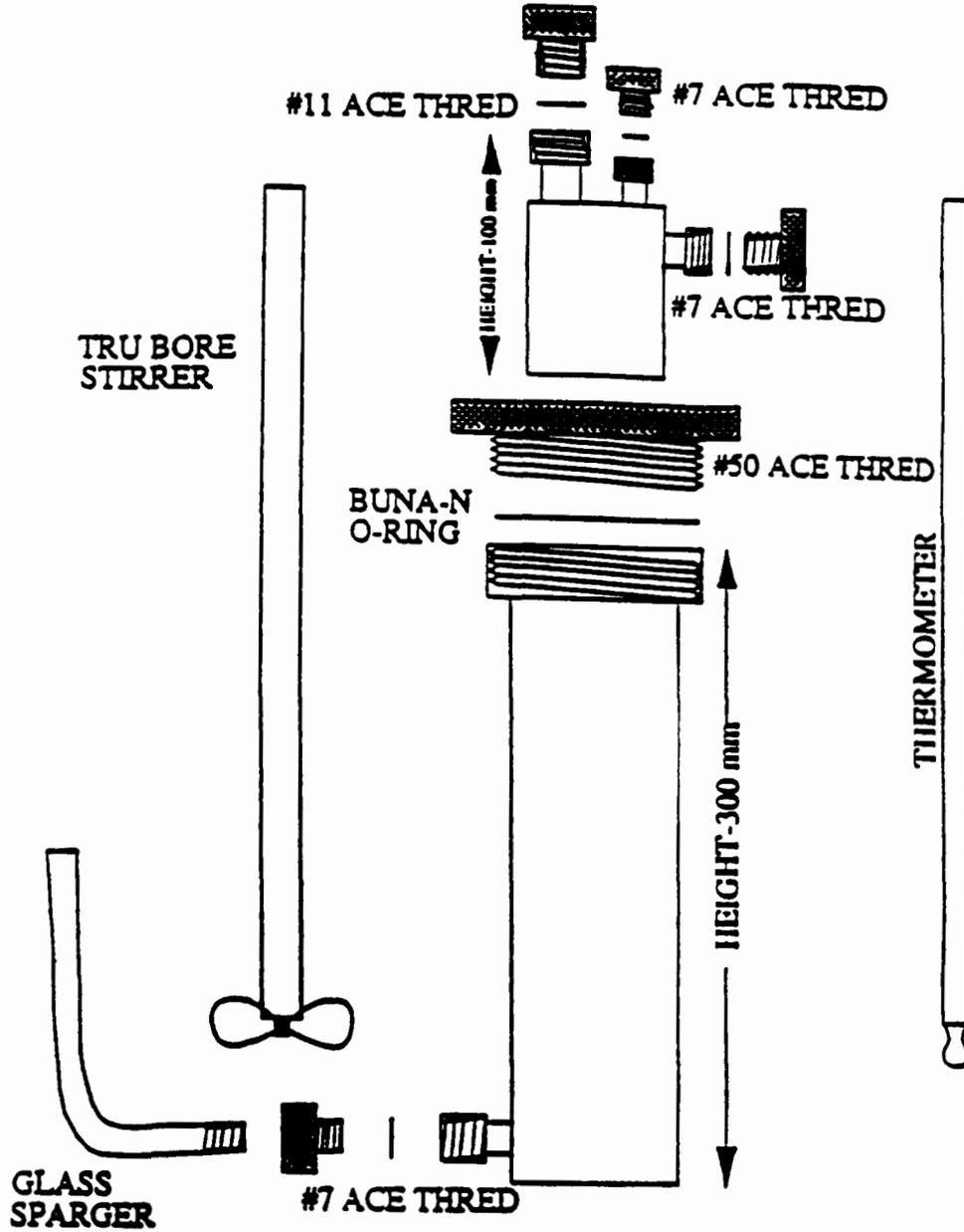
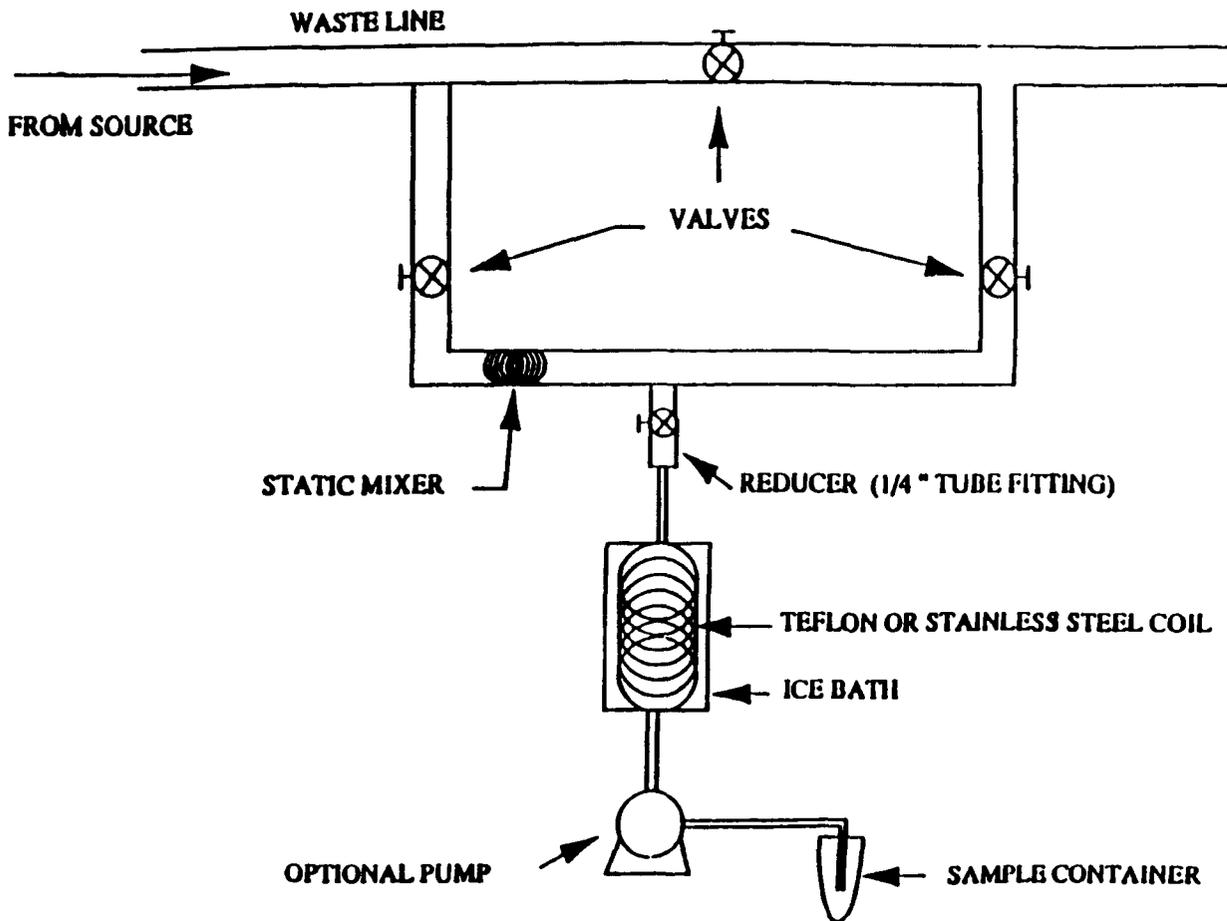
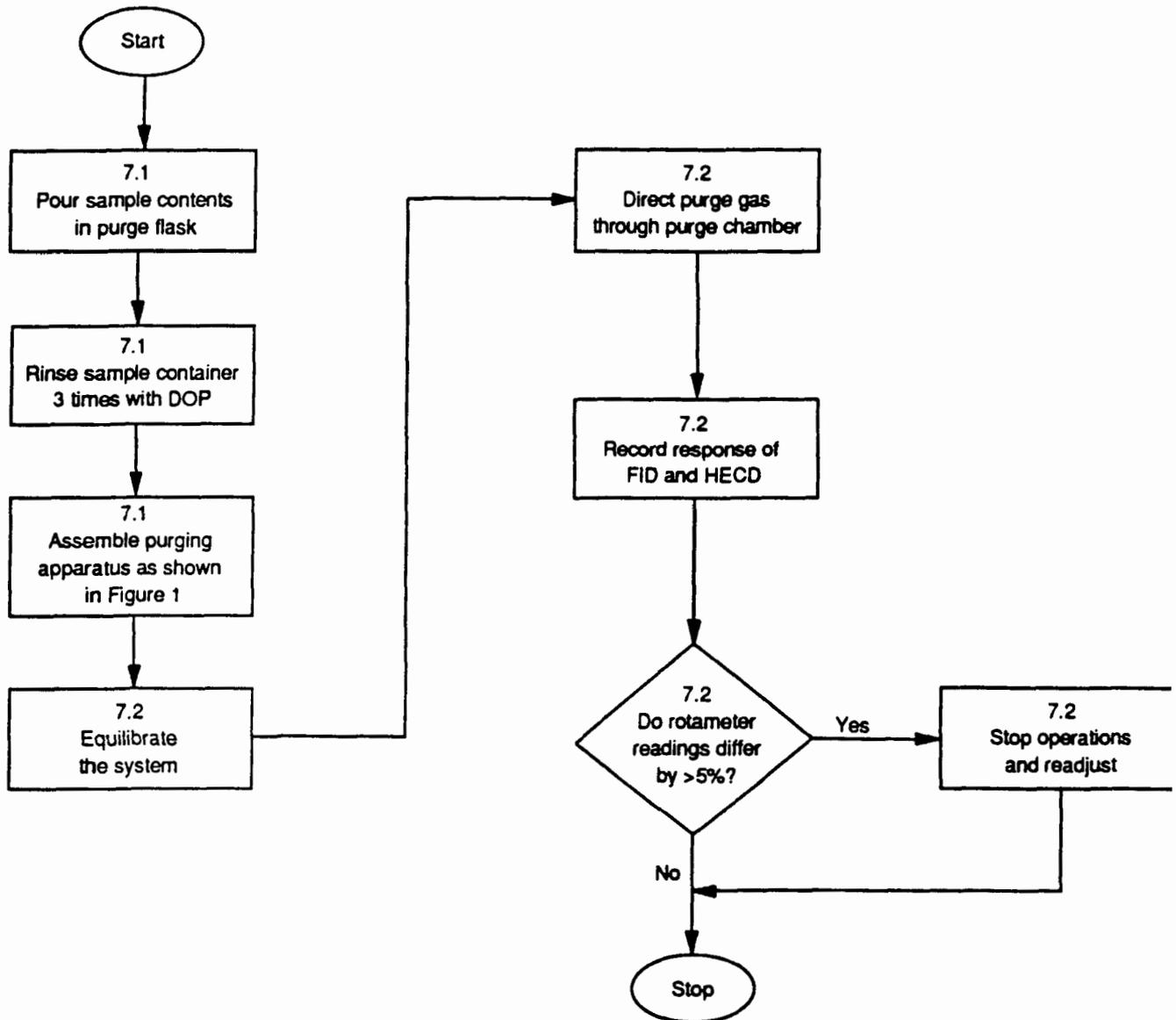


FIGURE 4



METHOD 5100
DETERMINATION OF THE VOLATILE ORGANIC CONCENTRATION OF WASTE SAMPLES



METHOD 5110

DETERMINATION OF ORGANIC PHASE VAPOR PRESSURE IN WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method is applicable for determining the organic phase vapor pressure of waste samples from treatment, storage, and disposal facilities (TSDF).

1.2 Performance of this method should not be attempted by persons unfamiliar with the operation of a Flame Ionization Detector (FID) nor by those who are unfamiliar with source sampling, because knowledge beyond the scope of this presentation is required.

2.0 SUMMARY OF METHOD

2.1 A waste sample is collected from a source as close to the point of generation as practical. The headspace vapor of the sample is analyzed for carbon content by a headspace analyzer, which uses an FID.

3.0 INTERFERENCES

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

3.2 Contamination by carryover can occur whenever a low-concentration sample is analyzed after a high-concentration sample. To reduce carryover, the sample syringe must be rinsed out between samples with organic-free reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 150°C oven between analyses.

3.3 Before processing daily samples, the analyst should demonstrate that the entire analytical system is free from interference by the analysis of an organic-free reagent water or solvent blank.

4.0 APPARATUS AND MATERIALS

4.1 Sampling. The following equipment is required:

4.1.1 Sample Containers. Vials, glass, with butyl rubber septa, Perkin-Elmer Corporation Part Numbers 0105-0129 (glass vials), B001-0728 (gray butyl rubber septa, plug style), 0105-0131 (butyl rubber septa), or equivalent. The seal must be made from butyl rubber. Silicone rubber seals are not acceptable.

4.1.2 Vial Sealer. Perkin-Elmer Number 105-0106, or equivalent.

4.1.3 Gas-Tight Syringe. Perkin-Elmer Number 00230117, or equivalent.

4.2 The following equipment is required if sampling from an enclosed pipe:

4.2.1 Static Mixer. Installed in-line or as a by-pass loop, sized so that the drop size of the dispersed phase is not greater than 1,000 μm . If the installation of the mixer is in a by-pass loop, then the entire waste stream must be diverted through the mixer.

4.2.2 Tap.

4.2.3 Tubing, Teflon, 0.25 in. ID.

4.2.4 Cooling Coil. Stainless steel (304), 0.25 in. ID, equipped with a thermocouple at the coil outlet.

4.3 Analysis. The following equipment is required:

4.3.1 Balanced Pressure Headspace Sampler. Perkin-Elmer HS-6, HS-100, or equivalent, equipped with a glass bead column instead of a chromatographic column.

4.3.2 Flame Ionization Detector. An FID meeting the following specifications is required:

4.3.2.1 Linearity. A linear response (± 5 percent) over the operating range, as demonstrated by the procedures established in Sections 7.2.2 and 8.1.1.

4.3.2.2 Range. A full scale range of 1 to 10,000 ppm CH_4 . Signal attenuators should be available to produce a minimum signal response of 10 percent of full scale.

4.3.3 Data Recording System. Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the output of the detector.

4.3.4 Thermometer. Capable of reading temperatures in the range of 30° to 60°C with an accuracy of $\pm 0.1^\circ\text{C}$.

5.0 REAGENTS

5.1 Analysis. The following reagents are required for analysis:

5.1.1 Hydrogen (H_2). Zero grade.

5.1.2 Carrier Gas. Zero grade nitrogen, containing less than 1 ppm carbon and less than 1 ppm carbon dioxide.

5.1.3 Combustion Gas. Zero grade air or oxygen, as required by the FID.

5.2 Calibration and Linearity Check.

5.2.1 Stock Cylinder Gas Standard. 100 percent propane. The manufacturer shall (a) certify the gas composition to be accurate to ± 3 percent or better (see Section 5.2.1.1); (b) recommend a maximum shelf life over which the gas concentration does not change by greater than ± 5 percent from the certified value; and (c) affix the date of gas cylinder preparation, certified propane concentration, and recommended maximum shelf life to the cylinder before shipment to the buyer.

5.2.1.1 Cylinder Standards Certification. The manufacturer shall certify the concentration of the calibration gas in the cylinder by (a) directly analyzing the cylinder and (b) calibrating his analytical procedure on the day of cylinder analysis. To calibrate his analytical procedure, the manufacturer shall use, as a minimum, a three-point calibration curve.

5.2.1.2 Verification of Manufacturer's Calibration Standards. Before using, the manufacturer shall verify the concentration of each calibration standard by (a) comparing it to gas mixtures prepared in accordance with the procedure described in Section 7.1 of Method 106 of 40 CFR Part 61, Appendix B, or by (b) calibrating it against Standard Reference Materials (SRMs), prepared by the National Institute of Science and Technology, if such SRMs are available. The agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent. The manufacturer must reverify all calibration standards on a time interval that is consistent with the shelf life of the cylinder standards sold.

5.3 Blanks

5.3.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

6.2 Sampling Plan Design and Development. Use the procedures given in Chapter Nine, "Sampling Plan."

6.3 Collect samples according to the procedures in Chapter 9, or, if it is necessary to sample from an enclosed pipe, sample according to the procedures described below.

6.3.1 The apparatus designed to sample from an enclosed pipe is shown in Figure 1. The apparatus consists of an in-line static mixer, a tap, a cooling coil immersed in an ice bath, a flexible Teflon tube

connected to the outlet of the cooling coil, and sample container. Locate the tap within two pipe diameters of the static mixer outlet. Install the static mixer in the process line or in a by-pass line.

6.3.2 Begin sample collection by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container.

6.3.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is $<10^{\circ}\text{C}$. Fill the sample container halfway (± 5 percent) and cap immediately (within 5 seconds).

6.3.4 Store the collected samples on ice or in a refrigerator until analysis.

6.3.5 Alternative sampling techniques may be used upon the approval of the Administrator.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Maintain a record of each item.

7.1.2 Use the procedures in Section 7.1.3 to calibrate the headspace analyzer and FID, and to check for linearity before the system is first placed in operation, after any shutdown that is longer than 6 months, and after any modification of the system.

7.1.3 Calibration and Linearity. Use the procedures in Section 6.2.1 of Method 18 of 40 CFR Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (± 5 percent) with organic-free reagent water. Prepare a minimum of three concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa (0.75 psi), prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa (4.0 psi), prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.

7.1.3.1 Use the procedures in Section 7.2.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y -intercept (b). Use the procedures in Section 7.2 and 7.3 to test the calibration and the linearity.

7.1.4 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare two calibration standards at the nominal cutoff concentrations using the procedures in Section 7.1.3. Place one at the beginning and end of the daily run. Measure the FID response of the daily calibration standard. Use the values for k and b obtained from the most recent calibration and use Equation 4 to calculate the concentration of

the daily standard. Use an equation similar to Equation 2 to calculate the percent difference between the daily standard and C_s . If the percent difference is within five, then the previous values for k and b can be used. Otherwise, use the procedures in Section 7.1.3 to recalibrate the FID.

7.2 Analysis.

7.2.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm until a stable baseline is achieved on the detector.

7.2.2 Check the calibration of the FID daily, using the procedures in Section 7.1.4.

7.2.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.

7.2.4 Use the procedures in Sections 7.3.4 and 7.3.5 to calculate the organic vapor pressure in the samples.

7.2.5 Monitor the output of the detector to make certain that the results are being properly recorded.

7.3 Calculations

7.3.1 Nomenclature

A	=	Measurement of the area under the response curve, counts.
b	=	y-intercept of the linear regression line.
C_a	=	Measured vapor phase organic concentration of sample, ppm as propane.
C_{ma}	=	Average measured vapor phase organic concentration of standard, ppm as propane.
C_m	=	Measured vapor phase organic concentration of standard, ppm as propane.
C_s	=	Calculated standard concentration, ppm as propane.
k	=	Slope of the linear regression line.
P_{bar}	=	Atmosphere pressure at analysis conditions, mm Hg (in. Hg).
p^*	=	Organic vapor pressure in the sample, kPa (psi).
β	=	1.333×10^{-6} kPa/[(mm Hg)(ppm)], 4.91×10^{-7} psi/[(in.Hg)(ppm)]

7.3.2 Linearity. Use Equation 1 to calculate the measured standard concentration for each standard vial.

$$c_m = k A + b \quad \text{Eq. 1}$$

7.3.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards, and use Equation 2 to calculate the percent difference between C_{ma} and C_s .

$$\text{Percent Difference} = \frac{C_s - C_{ma}}{C_s} \times 100 \quad \text{Eq. 2}$$

The instrument linearity is acceptable if the percent difference is less than or equal to five for each standard.

7.3.3 Relative standard Deviation (RSD). Use Equation 3 to calculate the RSD for each triplicate set of standards.

$$\%RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum_{i=1}^n (C_m - C_{ma})^2}{(n - 1)}} \quad \text{Eq. 3}$$

The calibration is acceptable if the RSD is within five percent for each standard concentration.

7.3.4 Concentration of Organics in the Headspace. Use Equation 4 to calculate the concentration of vapor phase organics in each sample.

$$C_a = k A + b \quad \text{Eq. 4}$$

7.3.5 Vapor Pressure of Organics in the Headspace. Use Equation 5 to calculate the vapor pressure of organics in the sample.

$$P^* = B P_{bar} C_a \quad \text{Eq. 5}$$

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific Quality Control procedures.

8.2 Maintain a record of performance of all system checks and calibrations.

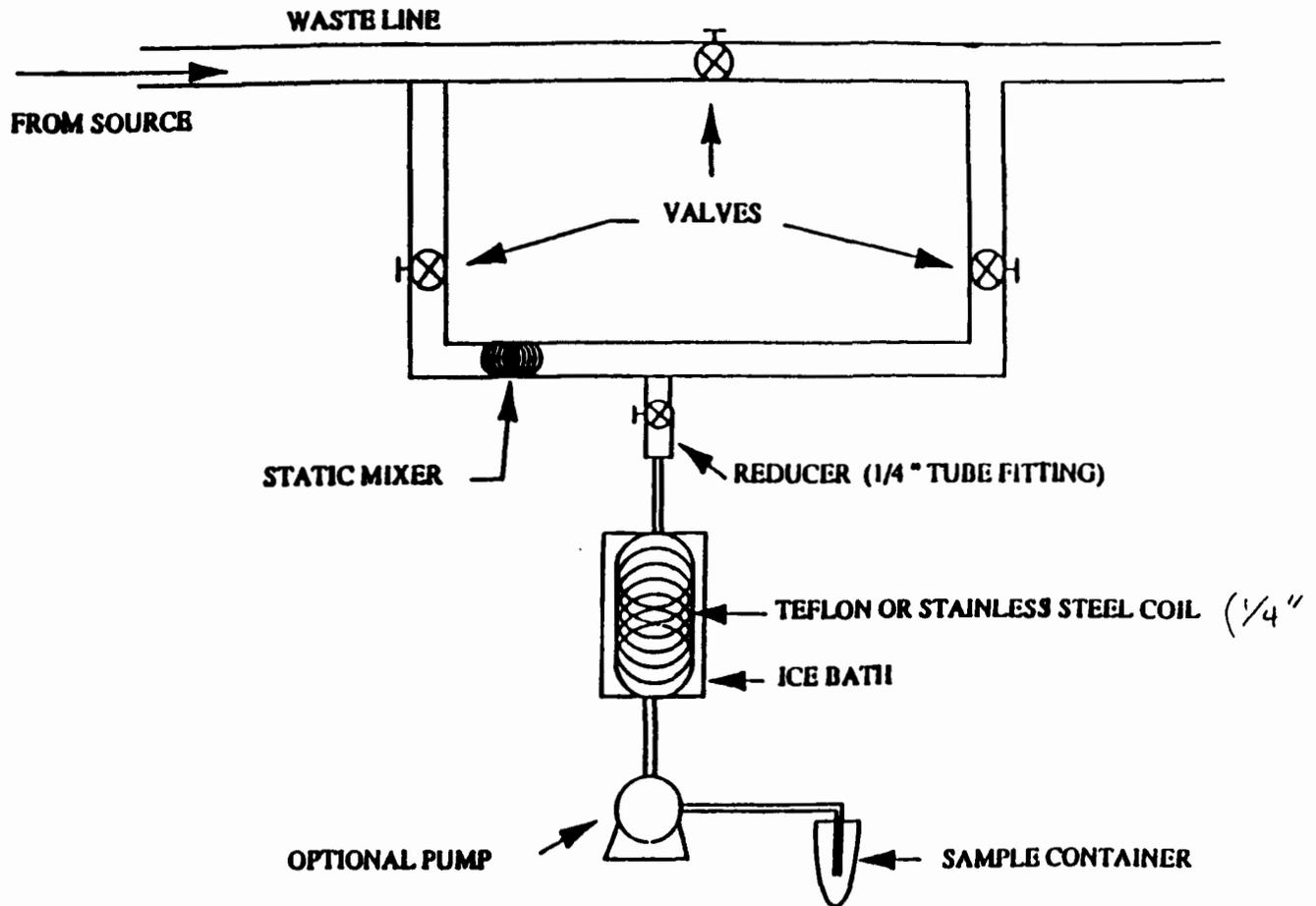
9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

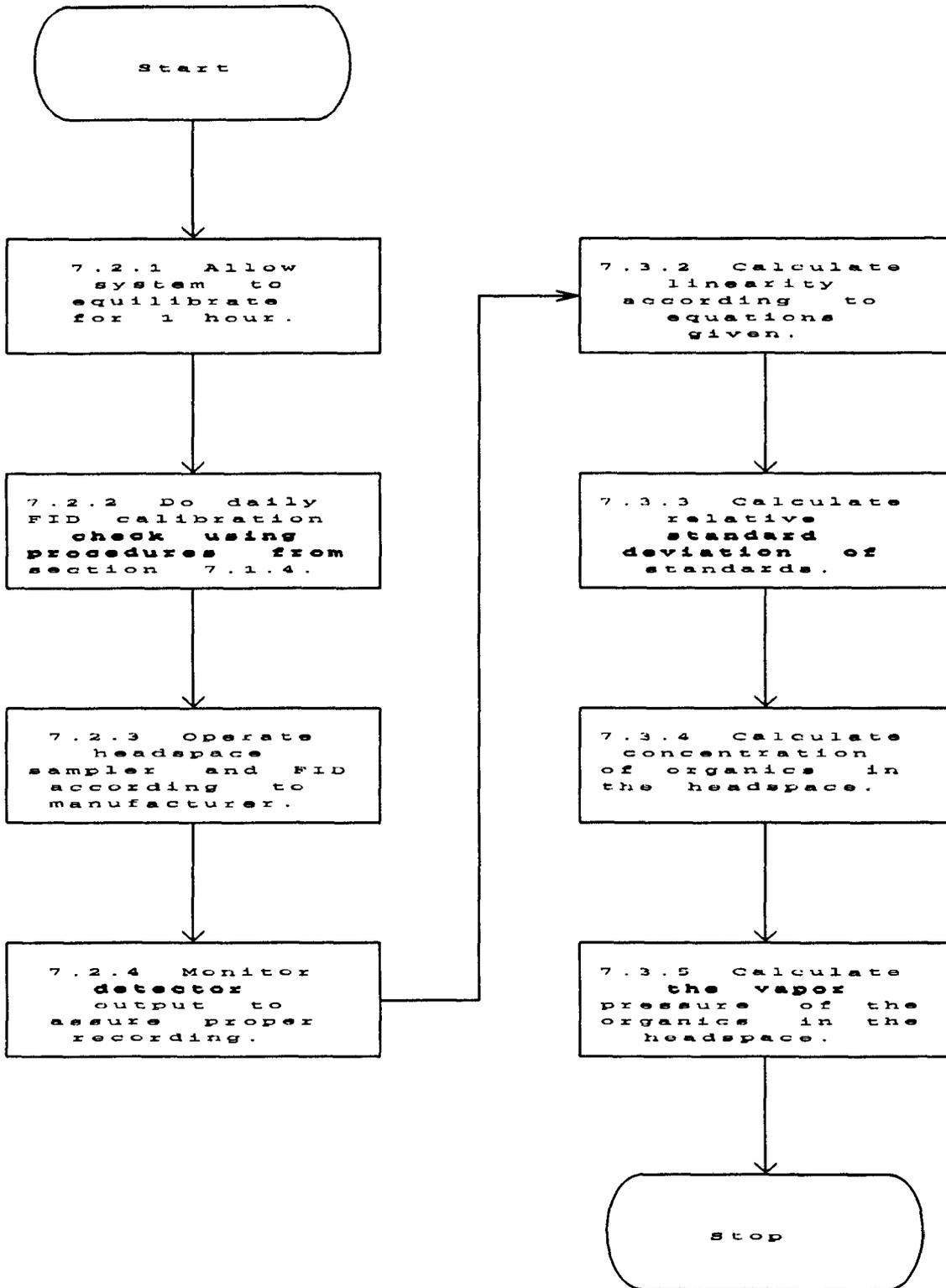
10.0 REFERENCES

1. "Determination of Vapor Phase Organic Concentrations in Waste Samples," Method 25E; Proposed Amendment to 40 CFR Part 60, Appendix A, January 1989.
2. "Headspace," Method 3810; U.S. Environmental Protection Agency, SW-846, 3rd Ed., 1986.

FIGURE 1



METHOD 5110
DETERMINATION OF ORGANIC PHASE VAPOR PRESSURE IN WASTE SAMPLES



METHOD 3600B

CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3600 provides general guidance on selection of cleanup methods that are appropriate for the target analytes of interest. Cleanup methods are applied to the extracts prepared by one of the extraction methods, to eliminate sample interferences. The following table lists the cleanup methods and provides a brief description of the type of cleanup.

SW-846 CLEANUP METHODS

<u>Method #</u>	<u>Method Name</u>	<u>Cleanup Type</u>
3610	Alumina Cleanup	Adsorption
3611	Alumina Cleanup & Separation for Petroleum Waste	Adsorption
3620	Florisil Cleanup	Adsorption
3630	Silica Gel Cleanup	Adsorption
3640	Gel-Permeation Cleanup	Size-Separation
3650	Acid-Base Partition Cleanup	Acid-Base Partitioning
3660	Sulfur Cleanup	Oxidation/Reduction
3665	Sulfuric Acid/Permanganate Cleanup	Oxidation/Reduction

1.2 The purpose of applying a cleanup method to an extract is to remove interferences and high boiling material that may result in: (1) errors in quantitation (data may be biased low because of analyte adsorption in the injection port or front of the GC column or biased high because of overlap with an interference peak); (2) false positives because of interference peaks falling within the analyte retention time window; (3) false negatives caused by shifting the analyte outside the retention time window; (4) rapid deterioration of expensive capillary columns; and, (5) instrument downtime caused by cleaning and rebuilding of detectors and ion sources. Most extracts of soil and waste require some degree of cleanup, whereas, cleanup for water extracts may be unnecessary. Highly contaminated extracts (e.g. sample extracts of oily waste or soil containing oily residue) often require a combination of cleanup methods. For example, when analyzing for organochlorine pesticides and PCBs, it may be necessary to use gel permeation chromatography (GPC), to eliminate the high boiling material and a micro alumina or Florisil column to eliminate interferences with the analyte peaks on the GC/ECD.

1.3 The following techniques have been applied to extract purification: adsorption chromatography; partitioning between immiscible solvents; gel permeation chromatography; oxidation of interfering substances with acid, alkali, or oxidizing agents. These techniques may be used individually or in various combinations, depending on the extent and nature of the co-extractives.

1.3.1 Adsorption column chromatography - Alumina (Methods 3610 and 3611), Florisil (Method 3620), and silica gel (Method 3630) are useful for separating analytes of a relatively narrow polarity range away from extraneous, interfering peaks of a different polarity. These are primarily used for cleanup of a specific chemical group of relatively non-polar analytes, i.e., organochlorine pesticides, polynuclear aromatic hydrocarbons (PAHs), nitrosamines, etc.. Solid phase extraction cartridges have been added as an option.

1.3.2 Acid-base partitioning (Method 3650) - Useful for separating acidic or basic organics from neutral organics. It has been applied to analytes such as the chlorophenoxy herbicides and phenols. It is very useful for separating the neutral PAHs from the acidic phenols when analyzing a site contaminated with creosote and pentachlorophenol.

1.3.3 Gel permeation chromatography (GPC) (Method 3640) - The most universal cleanup technique for a broad range of semivolatile organics and pesticides. It is capable of separating high molecular-weight, high boiling material from the sample analytes. It has been used successfully for all the semivolatile base, neutral, and acid compounds associated with the EPA Priority Pollutant and the Superfund Target Compound list prior to GC/MS analysis for semivolatiles and pesticides. GPC may not be applicable to elimination of extraneous peaks on a chromatogram which interfere with the analytes of interest. It is, however, useful for the removal of high boiling materials which would contaminate injection ports and column heads, prolonging column life, stabilizing the instrument, and reducing column reactivity.

1.3.4 Sulfur cleanup (Method 3660) - Useful in eliminating sulfur from sample extracts, which may cause chromatographic interference with analytes of interest.

1.4 Several of the methods are also useful for fractionation of complex mixtures of analytes. Use the solid phase extraction cartridges in Method 3630 (Silica Gel) for separating the PCBs away from most organochlorine pesticides. Method 3611 (Alumina) is for the fractionation of aliphatic, aromatic and polar analytes. Method 3620 (Florisil) provides fractionation of the organochlorine pesticides.

1.5 Cleanup capacity is another factor that must be considered in choosing a cleanup technique. The adsorption methods (3610, 3620, and 3630) provide the option of using standard column chromatography techniques or solid phase extraction cartridges. The decision process in selecting between the different options available generally depends on the amount of interferences/high boiling material in the sample extract and the degree of cleanup required by the determinative method. The solid phase extraction cartridges require less elution solvent and less time, however, their cleanup capacity is drastically reduced when comparing a 0.5 or 1.0 g Florisil cartridge to a 20 g standard Florisil

column. The same factor enters into the choice of the 70 g gel permeation column specified in Method 3640 versus a high efficiency column.

1.6 Table 1 indicates the recommended cleanup techniques for the indicated groups of compounds. This information can also be used as guidance for compounds that are not listed. Compounds that are chemically similar to these groups of compounds should behave similarly when taken through the cleanup procedure, however, this must be demonstrated by determining recovery of standards taken through the method.

2.0 SUMMARY OF METHOD

2.1 Refer to the specific cleanup method for a summary of the procedure.

3.0 INTERFERENCES

3.1 Analytical interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free of interferences, under the conditions of the analysis, by running laboratory reagent blanks.

3.2 More extensive procedures than those outlined in the methods may be necessary for reagent purification.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific cleanup method for apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific cleanup method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples normally undergo solvent extraction. Chapter Two, Section 2.0, may be used as a guide for choosing the appropriate extraction procedure based on the physical composition of the waste and on the analytes of interest in the matrix (see also Method 3500 for a general description of the extraction technique). For some organic liquids, extraction prior to cleanup may not be necessary.

7.2 Most soil/sediment and waste sample extracts will require some degree of cleanup. The extract is then analyzed by one of the determinative methods. If interferences still preclude analysis for the analytes of interest, additional cleanup may be required.

7.3 Many of the determinative methods specify cleanup methods that should be used when determining particular analytes (e.g. Method 8060, gas chromatography of phthalate esters, recommends using either Method 3610 (Alumina column cleanup) or Method 3620 (Florisil column cleanup) if interferences prevent analysis. However, the experience of the analyst may prove invaluable in determining which cleanup methods are needed. As indicated in Section 1.0 of this method, many matrices may require a combination of cleanup procedures in order to ensure proper analytical determinations.

7.4 Guidance for cleanup is specified in each of the methods that follow. The amount of extract cleanup required prior to the final determination depends on the concentration of interferences in the sample, the selectivity of both the extraction procedure and the determinative method and the required detection limit.

7.5 Following cleanup, the sample is concentrated to whatever volume is required in the determinative method. Analysis follows as specified in the determinative procedure.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 The analyst must demonstrate that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples. For sample extracts that are cleaned up, the associated quality control samples (e.g. spikes, blanks, replicates, and duplicates) must also be processed through the same cleanup procedure.

8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

9.0 METHOD PERFORMANCE

9.1 Refer to the specific cleanup method for performance data.

10.0 REFERENCES

10.1 Refer to the specific cleanup method.

TABLE 1.
RECOMMENDED CLEANUP TECHNIQUES FOR INDICATED GROUPS OF COMPOUNDS

Analyte Group	Determinative ^a Method	Cleanup Method Options
Phenols	8040	3630 ^b , 3640, 3650, 8040 ^c
Phthalate esters	8060/8061	3610, 3620, 3640
Nitrosamines	8070	3610, 3620, 3640
Organochlorine pesticides & PCBs	8080/8081	3620, 3640, 3660
PCBs	8080/8081	3665
Nitroaromatics and cyclic ketones	8090	3620, 3640
Polynuclear aromatic hydrocarbons	8100/8310	3611, 3630, 3640
Chlorinated hydrocarbons	8120/8121	3620, 3640
Organophosphorus pesticides	8140/8141	3620
Chlorinated herbicides	8150/8151	8150 ^d , 3620
Semivolatile organics	8250/8270	3640, 3650, 3660
Petroleum waste	8250/8270	3611, 3650
PCDDs and PCDFs by LR/MS	8280	8280
PCDDs and PCDFs by HR/MS	8290	8290
N-methyl carbamate pesticides	8318	8318

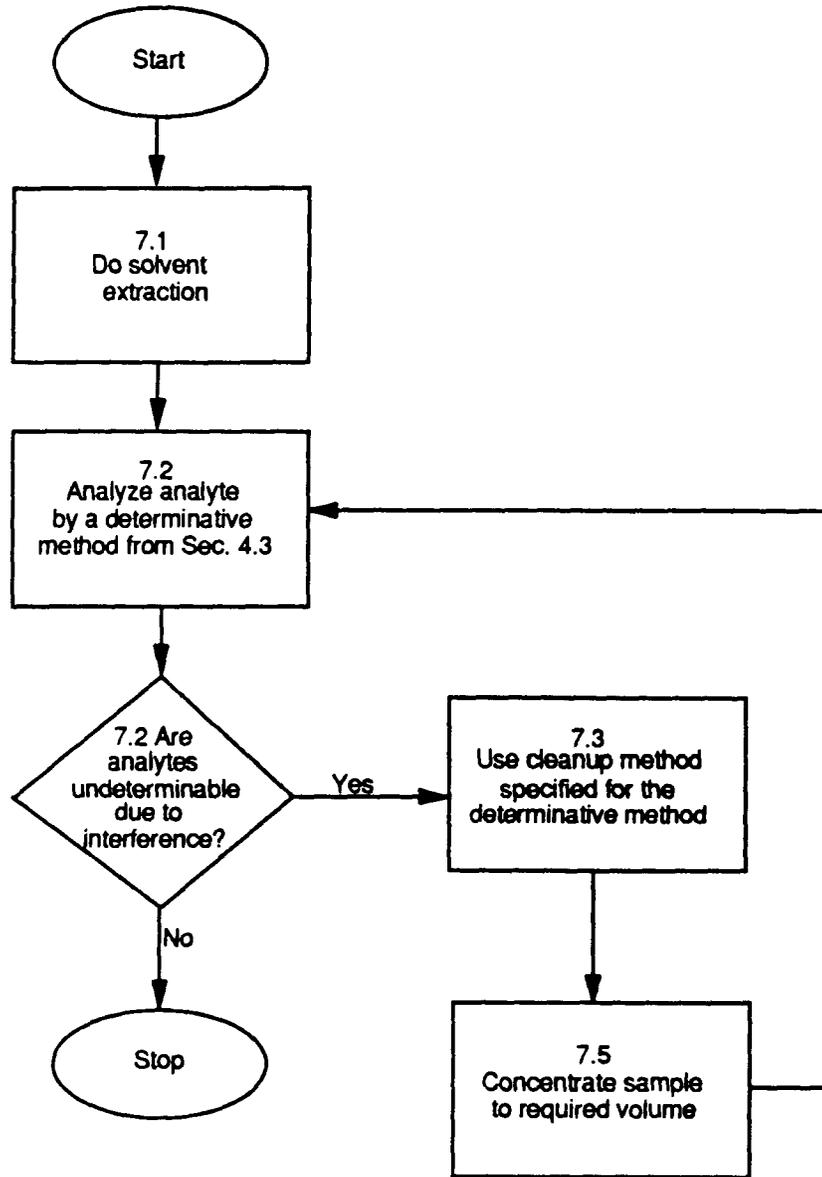
^a The GC/MS Methods, 8250 and 8270, are also appropriate determinative methods for all analyte groups, unless lower detection limits are required.

^b Cleanup applicable to derivatized phenols.

^c Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered using GC/FID.

^d Method 8150 incorporates an acid-base cleanup step as an integral part of the method.

METHOD 3600B
CLEANUP



METHOD 3630B

SILICA GEL CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Silica gel is a regenerative adsorbent of amorphous silica with weakly acidic properties. It is produced from sodium silicate and sulfuric acid. Silica gel can be used in column chromatography for the separation of analytes from interfering compounds of a different chemical polarity. It may be used activated after heating to 150 - 160°C or deactivated with up to 10% water.

1.2 This method includes guidance for standard column cleanup of sample extracts containing polynuclear aromatic hydrocarbons, derivatized phenolic compounds, organochlorine pesticides and, PCBs as Aroclors.

1.3 This method also provides cleanup procedures using solid-phase extraction cartridges for pentafluorobenzyl bromide derivatized phenols and organochlorine pesticides/PCBs as Aroclors. This technique also provides the best separation of PCBs from most single component organochlorine pesticides. When only PCBs are to be measured, this method can be used in conjunction with sulfuric acid/permanganate cleanup (Method 3665).

1.4 Other analytes may be cleaned up using this method if the analyte recovery meets the criteria specified in Section 8.0.

2.0 SUMMARY OF METHOD

2.1 This method provides the option of using either standard column chromatography techniques or solid-phase extraction cartridges. Generally, the standard column chromatography techniques use larger amounts of adsorbent and, therefore, have a greater cleanup capacity.

2.2 In the standard column cleanup protocol, the column is packed with the required amount of adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution of the analytes is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated (if necessary).

2.3 The cartridge cleanup protocol uses silica solid-phase extraction cartridges packed with 1 g or 2 g of adsorbent. Each cartridge is solvent washed immediately prior to use. Aliquots of sample extracts are loaded onto the cartridges which are then eluted with suitable solvent(s). A vacuum manifold is required to obtain reproducible results. The collected fractions may be further concentrated prior to gas chromatographic analysis.

2.4 The appropriate gas chromatographic method is listed at the end of each technique. Analysis may also be performed by gas chromatography/mass spectrometry (Method 8270).

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All these materials must be demonstrated to be free from interferences under the conditions of the analysis, by analyzing reagent blanks. See Section 8 for guidance on a reagent blank check.

3.2 Phthalate ester contamination may be a problem with certain cartridges. The more inert the column and/or cartridge material (i.e., glass or Teflon), the less problem with phthalates. Phthalates create interference problems for all method analytes, not just the phthalate esters themselves.

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

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column - 250 mm long x 10 mm ID; with Pyrex glass wool at bottom and a Teflon stopcock.

NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.2 Beakers - 500 mL.

4.3 Vials - 2, 10, 25 mL, glass with Teflon lined screw-caps or crimp tops.

4.4 Muffle furnace.

4.5 Reagent bottle - 500 mL.

4.6 Erlenmeyer flasks - 50 and 250 mL.

4.7 Vacuum manifold: VacElute Manifold SPS-24 (Analytichem International), Visiprep (Supelco, Inc.) or equivalent, consisting of glass vacuum basin, collection rack and funnel, collection vials, replaceable stainless steel delivery tips, built-in vacuum bleed valve and gauge. The system is connected to a vacuum pump or water aspirator through a vacuum trap made from a 500 mL sidearm flask fitted with a one-hole stopper and glass tubing.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first

ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Silica gel for chromatography columns.

5.3.1 Silica Gel for Phenols and Polynuclear Aromatic Hydrocarbons: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil.

5.3.2 Silica Gel for Organochlorine pesticides/PCBs: 100/200 mesh desiccant (Davison Chemical grade 923 or equivalent). Before use, activate for at least 16 hr. at 130°C in a shallow glass tray, loosely covered with foil. Deactivate it to 3.3% with reagent water in a 500 mL glass jar. Mix the contents thoroughly and allow to equilibrate for 6 hours. Store the deactivated silica gel in a sealed glass jar inside a desiccator.

5.4 Silica cartridges: 40 µm particles, 60 A pores. The cartridges from which this method were developed consist of 6 mL serological-grade polypropylene tubes, with the 1 g of silica held between two polyethylene or stainless steel frits with 20 µm pores. 2 g silica cartridges are also used in this method, and 0.5 g cartridges are available. The compound elution patterns must be verified when cartridges other than the specified size are used.

5.5 Sodium sulfate (granular, anhydrous), Na₂SO₄. Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. A method blank must be analyzed in order to demonstrate that there is no interference from the sodium sulfate.

5.6 Eluting solvents

5.6.1 Cyclohexane, C₆H₁₂ - Pesticide quality or equivalent.

5.6.2 Hexane, C₆H₁₄ - Pesticide quality or equivalent.

5.6.3 2-Propanol, (CH₃)₂CHOH - Pesticide quality or equivalent.

5.6.4 Toluene, C₆H₅CH₃ - Pesticide quality or equivalent.

5.6.5 Methylene chloride, CH₂Cl₂ - Pesticide quality or equivalent.

5.6.6 Pentane, C₅H₁₂ - Pesticide quality or equivalent.

5.6.7 Acetone, CH₃COCH₃ - Pesticide quality or equivalent.

5.6.8 Diethyl Ether, C₂H₅OC₂H₅. Pesticide quality or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethanol preservative must be added to each liter of ether.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 General Guidance

7.1.1 The procedure contains two cleanup options for the derivatized phenols and organochlorine pesticides/Aroclors, but only one technique for the polynuclear aromatic hydrocarbons (PAHs) (standard column chromatography). Cleanup techniques by standard column chromatography for all analytes are found in Section 7.2. Cleanup techniques by solid-phase cartridges for derivatized phenols and PAHs are found in Section 7.3. The standard column chromatography techniques are packed with a greater amount of silica gel adsorbent and, therefore, have a greater cleanup capacity. A rule of thumb relating to cleanup capacity is that 1 g of sorbent material will remove 10 to 30 mg of total interferences. (However, capacity is also dependent on the sorbent retentiveness of the interferences.) Therefore, samples that exhibit a greater degree of sample interference should be cleaned up by this technique. However, both techniques have limits on the amount of interference that can be removed. If the interference is caused by high boiling material, then Method 3640 should be used prior to this method. If the interference is caused by relatively polar compounds of the same boiling range as the analytes, then multiple column or cartridge cleanups may be required. If crystals of sulfur are noted in the extract, then Method 3660 should be utilized prior to this method. The cartridge cleanup techniques are often faster and use less solvent, however they have less cleanup capacity.

7.1.2 Allow the extract to reach room temperature if it was in cold storage. Inspect the extracts visually to ensure that there are no particulates or phase separations and that the volume is as stated in the accompanying documents. Verify that the solvent is compatible with the cleanup procedures. If crystals of sulfur are visible or if the presence of sulfur is suspected, proceed with Method 3660.

7.1.3 The extract solvent for most cleanup techniques must be exchanged to hexane if it is in methylene chloride. (For the PAHs, exchange to cyclohexane as per Section 7.2.1). Follow the standard Kuderna-Danish concentration technique provided in each extraction method. The volume of methylene chloride should have been reduced to 1 - 2 mL. Add 40 mL of hexane, a fresh boiling chip and repeat the concentration as written. The final volume required for the cleanup techniques is normally 2 mL.

7.2 Standard Column Cleanup Techniques

7.2.1 Polynuclear aromatic hydrocarbons

7.2.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. The

exchange is performed by adding 4 mL of cyclohexane following reduction of the sample extract to 1-2 mL using the macro Snyder column. Attach the two ball micro Snyder column and reduce the volume to 2 mL.

CAUTION: When the volume of solvent is reduced below 1 mL, semivolatile analytes may be lost. If the extract goes to dryness, the extraction must be repeated.

7.2.1.2 Prepare a slurry of 10 g of activated silica gel (Section 5.3.1) in methylene chloride and place this into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and elute the methylene chloride. Add 1 to 2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.2.1.3 Preelute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL cyclohexane sample extract onto the column using an additional 2 mL cyclohexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue the elution of the column. Discard this pentane eluate.

7.2.1.4 Next, elute the column with 25 mL of methylene chloride/pentane (2:3)(v/v) into a 500 mL K-D flask equipped with a 10 mL concentrator tube. Concentrate the collected fraction to whatever volume is required (1-10 mL). Proceed with HPLC (Method 8310) or GC analysis (Method 8100). Validated components that elute in this fraction are:

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(a)anthracene
- Benzo(a)pyrene
- Benzo(b)fluoranthene
- Benzo(g,h,i)perylene
- Benzo(k)fluoranthene
- Chrysene
- Dibenzo(a,h)anthracene
- Fluoranthene
- Fluorene
- Indeno(1,2,3-cd)pyrene
- Naphthalene
- Phenanthrene
- Pyrene

7.2.2 Derivatized Phenols

7.2.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040. The sample extract must

be in 2 mL of hexane at this point.

7.2.2.2 Place 4.0 g of activated silica gel (Section 5.3.1) into a 10 mm ID chromatographic column. Tap the column to settle the silica gel and add about 2 g of anhydrous sodium sulfate to the top of the silica gel.

7.2.2.3 Preeelute the column with 6 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and just prior to exposure of the sodium sulfate layer to the air, pipet onto the column 2 mL of the hexane solution that contains the derivatized sample or standard. Elute the column with 10.0 mL of hexane and discard the eluate.

7.2.2.4 Elute the column, in order, with 10.0 mL of 15% toluene in hexane (Fraction 1); 10.0 mL of 40% toluene in hexane (Fraction 2); 10.0 mL of 75% toluene in hexane (Fraction 3); and 10.0 mL of 15% 2-propanol in toluene (Fraction 4). All elution mixtures are prepared on a volume:volume basis. Elution patterns for the phenolic derivatives are shown in Table 1. Fractions may be combined, as desired, depending upon the specific phenols of interest or level of interferences. Proceed with GC analysis (Method 8040).

7.2.3 Organochlorine Pesticides and Aroclors

7.2.3.1 Transfer a 3 g portion of deactivated silica gel (Section 5.3.2) into a 10 mm ID glass chromatographic column and top it with 2 to 3 cm of anhydrous sodium sulfate.

7.2.3.2 Add 10 mL of hexane to the top of the column to wet and rinse the sodium sulfate and silica gel. Just prior to exposure of the sodium sulfate layer to air, stop the hexane eluate flow by closing the stopcock on the chromatographic column. Discard the eluate.

7.2.3.3 Transfer the sample extract (2 mL in hexane) onto the column. Rinse the extract vial twice with 1 to 2 mL of hexane and add each rinse to the column. Elute the column with 80 mL of hexane (Fraction I) at a rate of about 5 mL/min. Remove the collection flask and set it aside for later concentration. Elute the column with 50 mL of hexane (Fraction II) and collect the eluate. Perform a third elution with 15 mL of methylene chloride (Fraction III). The elution patterns for the organochlorine pesticides, Aroclor-1016, and Aroclor-1260 are shown in Table 2.

7.2.3.4 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. Fractions may be combined, as desired, depending upon the specific pesticides/Aroclors of interest or level of interferences. If mixtures of Aroclors and pesticides are expected, it is best to analyze Fraction I separately since it contains the Aroclors separated from most pesticides. Proceed with GC analysis as per Method 8080 or 8081.

7.3 Cartridge Cleanup Techniques

7.3.1 Cartridge Set-up and Conditioning

7.3.1.1 Arrange the 1 g Florisil cartridges (2 g for phenol cleanup) on the manifold in the closed-valve position. Other size cartridges may be used, however the data presented in the Tables is all based on 1 g cartridges for pesticides/Aroclors and 2 g cartridges for phenols. Therefore, supporting recovery data must be developed for other sizes. Larger cartridges will probably require larger volumes of elution solvents.

7.3.1.2 Turn vacuum pump on and set pump vacuum to 10 inches or 254 mm of Hg. Do not exceed the manufacturer's recommendation for manifold vacuum. Flow rates can be controlled by opening and closing cartridge valves.

7.3.1.3 Condition the cartridges by adding 4 mL of hexane to each cartridge. Slowly open the cartridge valves to allow hexane to pass through the sorbent beds to the lower frits. Allow a few drops per cartridge to pass through the manifold to remove all air bubbles. Close the valves and allow the solvent to soak the entire sorbent bed for 5 minutes. Do not turn off the vacuum.

7.3.1.4 Slowly open cartridge valves to allow the hexane to pass through the cartridges. Close the cartridge valves when there is still at least 1 mm of solvent above the sorbent bed. Do not allow cartridges to become dry. If cartridges go dry, repeat the conditioning step.

7.3.2 Derivatized Phenols

7.3.2.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane and the phenols must have undergone derivatization by pentafluorobenzyl bromide as per Methods 8040 or 8041.

7.3.2.2 Transfer the extract to the 2 g cartridge conditioned as described in Section 7.3.1. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.2.3 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of hexane, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.2.4 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never gets dry.

7.3.2.5 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover

and align with the collection vial.

7.3.2.6 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches or 254 mm of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve, and collect the eluate (this is Fraction 1, and should be discarded).

NOTE: If cartridges smaller than 2 g are used, then Fraction 1 cannot be discarded, since it contains some of the phenols.

7.3.2.7 Close the cartridge valve, replace the collection vial, and add 5 mL of toluene/hexane (25/75, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial. This is Fraction 2, and should be retained for analysis.

7.3.2.8 Adjust the final volume of the eluant to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL). Table 3 shows compound recoveries for 2 g silica cartridges. The cleaned up extracts are ready for analysis by Methods 8040 or 8041.

7.3.3 Organochlorine Pesticides/Aroclors

NOTE: The silica cartridge procedure is appropriate when polychlorinated biphenyls are known to be present.

7.3.3.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.3.3.2 Use the 1 g cartridges conditioned as described in Section 7.3.1.

7.3.3.3 Transfer the extract to the cartridge. Open the cartridge valve to allow the extract to pass through the cartridge bed at approximately 2 mL/minute.

7.3.3.4 When the entire extract has passed through the cartridges, but before the cartridge becomes dry, rinse the sample vials with an additional 0.5 mL of solvent, and add the rinse to the cartridges to complete the quantitative transfer.

7.3.3.5 Close the cartridge valve and turn off the vacuum after the solvent has passed through, ensuring that the cartridge never goes dry.

7.3.3.6 Place a 5 mL vial or volumetric flask into the sample rack corresponding to the cartridge position. Attach a solvent-rinsed stainless steel solvent guide to the manifold cover and align with the collection vial.

7.3.3.7 Add 5 mL of hexane to the cartridge. Turn on the vacuum pump and adjust the pump pressure to 10 inches or 254 mm of Hg. Allow the solvent to soak the sorbent bed for 1 minute or less. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 1).

7.3.3.8 Close the cartridge valve, replace the collection vial, and add 5 mL of diethyl ether/hexane (50/50, v/v) to the cartridge. Slowly open the cartridge valve and collect the eluate into the collection vial (Fraction 2).

7.3.3.9 Adjust the final volume of the two fractions to a known volume which will result in analyte concentrations appropriate for the project requirements (normally 1 - 10 mL). The fractions may be combined prior to final adjustment of volume, if analyte fractionation is not required. Table 4 shows compound recoveries for 1 g silica cartridges. The cleaned up extracts are ready for analysis by Methods 8080 or 8081.

3.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 A reagent blank (consisting of the elution solvents) must be passed through the column or cartridge and checked for the compounds of interest, prior to the use of this method. This same performance check is required with each new lot of adsorbent or cartridges. The level of interferences must be below the method detection limit before this method is performed on actual samples.

8.3 The analyst must demonstrate that the compounds of interest are being quantitatively recovered before applying this method to actual samples. See the attached Tables for acceptable recovery data. For compounds that have not been tested, recovery must be $\geq 85\%$.

8.3.1 Before any samples are processed using the solid-phase extraction cartridges, the efficiency of the cartridge must be verified. A recovery check must be performed using standards of the target analytes at known concentration. Only lots of cartridges that meet the recovery criteria for the spiked compounds can be used to process the samples.

8.3.2 A check should also be performed on each individual lot of cartridges and for every 300 cartridges of a particular lot.

8.4 For sample extracts that are cleaned up using this method, the associated quality control samples should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 provides performance information on the fractionation of phenolic derivatives using standard column chromatography.

9.2 Table 2 provides performance information on the fractionation of organochlorine pesticides/Aroclors using standard column chromatography.

9.3 Table 3 shows recoveries of derivatized phenols obtained using 2 g silica cartridges.

9.4 Table 4 shows recoveries and fractionation of organochlorine pesticides obtained using 1 g silica cartridges.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
2. U.S. EPA "Evaluation of Sample Extract Cleanup Using Solid-Phase Extraction Cartridges," Project Report, December 1989.

TABLE 1
SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

Parameter	Percent Recovery by Fraction ^a			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

^a Eluant composition:

- Fraction 1 - 15% toluene in hexane.
- Fraction 2 - 40% toluene in hexane.
- Fraction 3 - 75% toluene in hexane.
- Fraction 4 - 15% 2-propanol in toluene.

Data from Reference 1 (Method 604)

TABLE 2
 DISTRIBUTION AND PERCENT RECOVERIES OF ORGANOCHLORINE
 PESTICIDES AND PCBs AS AROCLORS IN SILICA GEL COLUMN FRACTIONS^{a,b,c,d,e}

Compound	Fraction I		Fraction II		Fraction III		Total Recovery	
	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.	Conc.
	1	2	1	2	1	2	1	2
alpha-BHC ^f					82(1.7)	74(8.0)	82(1.7)	74(8.0)
beta-BHC					107(2.1)	98(12.5)	107(2.1)	98(12.5)
gamma-BHC					91(3.6)	85(10.7)	91(3.6)	85(10.7)
delta-BHC					92(3.5)	83(10.6)	92(3.5)	83(10.6)
Heptachlor	109(4.1)	118(8.7)					109(4.1)	118(8.7)
Aldrin	97(5.6)	104(1.6)					97(5.6)	104(1.6)
Heptachlor epoxide					95(4.7)	88(10.2)	95(4.7)	88(10.2)
Technical chlordane	14(5.5)	22(5.3)	19(6.8)	39(3.6)	29(5.0)	37(5.1)	62(3.3)	98(1.9)
Endosulfan I					95(5.1)	87(10.2)	95(5.1)	87(10.2)
4,4'-DDE	86(5.4)	94(2.8)					86(5.4)	94(2.8)
Dieldrin					96(6.0)	87(10.6)	96(6.0)	87(10.6)
Endrin					85(10.5)	71(12.3)	85(10.5)	71(12.3)
Endosulfan II					97(4.4)	86(10.4)	97(4.4)	86(10.4)
4,4'-DDD ^f					102(4.6)	92(10.2)	102(4.6)	92(10.2)
Endrin aldehyde					81(1.9)	76(9.5)	81(1.9)	76(9.5)
Endosulfan sulfate					93(4.9)	82(9.2)	93(4.9)	82(9.2)
4,4'-DDT ^f			86(13.4)	73(9.1)	15(17.7)	8.7(15.0)	101(5.3)	82(23.7)
4,4'-Methoxychlor					99(9.9)	82(10.7)	99(9.9)	82(10.7)
Toxaphene ^f			15(2.4)	17(1.4)	73(9.4)	84(10.7)	88(12.0)	101(10.1)
Aroclor-1016	86(4.0)	87(6.1)					86(4.0)	87(6.1)
Aroclor-1260	91(4.1)	95(5.0)					91(4.1)	95(5.0)

TABLE 2
(Continued)

-
- ^a Effluent composition: Fraction I, 80 mL hexane; Fraction II, 50 mL hexane; Fraction III, 15 mL methylene chloride.
- ^b Concentration 1 is 0.5 μg per column for BHCs, heptachlor, aldrin, heptachlor epoxide, and endosulfan I; 1.0 μg per column for dieldrin, endosulfan II, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, endrin, endrin aldehyde, and endosulfan sulfate; 5 μg per column for 4,4'-methoxychlor and technical chlordane; 10 μg per column for toxaphene, Aroclor-1016, and Aroclor-1260.
- ^c For Concentration 2, the amounts spiked are 10 times as high as those for Concentration 1.
- ^d Values given represent the average recovery of three determinations; numbers in parentheses are the standard deviation; recovery cutoff point is 5 percent.
- ^e Data obtained with standards, as indicated in footnotes b and c, dissolved in 2 mL hexane.
- ^f It has been found that because of batch-to-batch variation in the silica gel material, these compounds cross over in two fractions and the amounts recovered in each fraction are difficult to reproduce.

TABLE 3
PERCENT RECOVERIES AND ELUTION PATTERNS FOR 18
PHENOLS FROM 2 g SILICA CARTRIDGES^a

Compound	Fraction 2	
	Average Recovery	Percent RSD
Phenol	74.1	5.2
2-Methylphenol	84.8	5.2
3-Methylphenol	86.4	4.4
4-Methylphenol	82.7	5.0
2,4-Dimethylphenol	91.8	5.6
2-Chlorophenol	88.5	5.0
2,6-Dichlorophenol	90.4	4.4
4-Chloro-3-methylphenol	94.4	7.1
2,4-Dichlorophenol	94.5	7.0
2,4,6-Trichlorophenol	97.8	6.6
2,3,6-Trichlorophenol	95.6	7.1
2,4,5-Trichlorophenol	92.3	8.2
2,3,5-Trichlorophenol	92.3	8.2
2,3,5,6-Tetrachlorophenol	97.5	5.3
2,3,4,6-Tetrachlorophenol	97.0	6.1
2,3,4-Trichlorophenol	72.3	8.7
2,3,4,5-Tetrachlorophenol	95.1	6.8
Pentachlorophenol	96.2	8.8

^a Silica cartridges (Supelco, Inc.) were used; each cartridge was conditioned with 4 mL of hexane prior to use. Each experiment was performed in duplicate at three spiking concentrations (0.05 µg, 0.2 µg, and 0.4 µg per compound per cartridge). Fraction 1 was eluted with 5 mL hexane and was discarded. Fraction 2 was eluted with 5 mL toluene/hexane (25/75, v/v).

Data from Reference 2

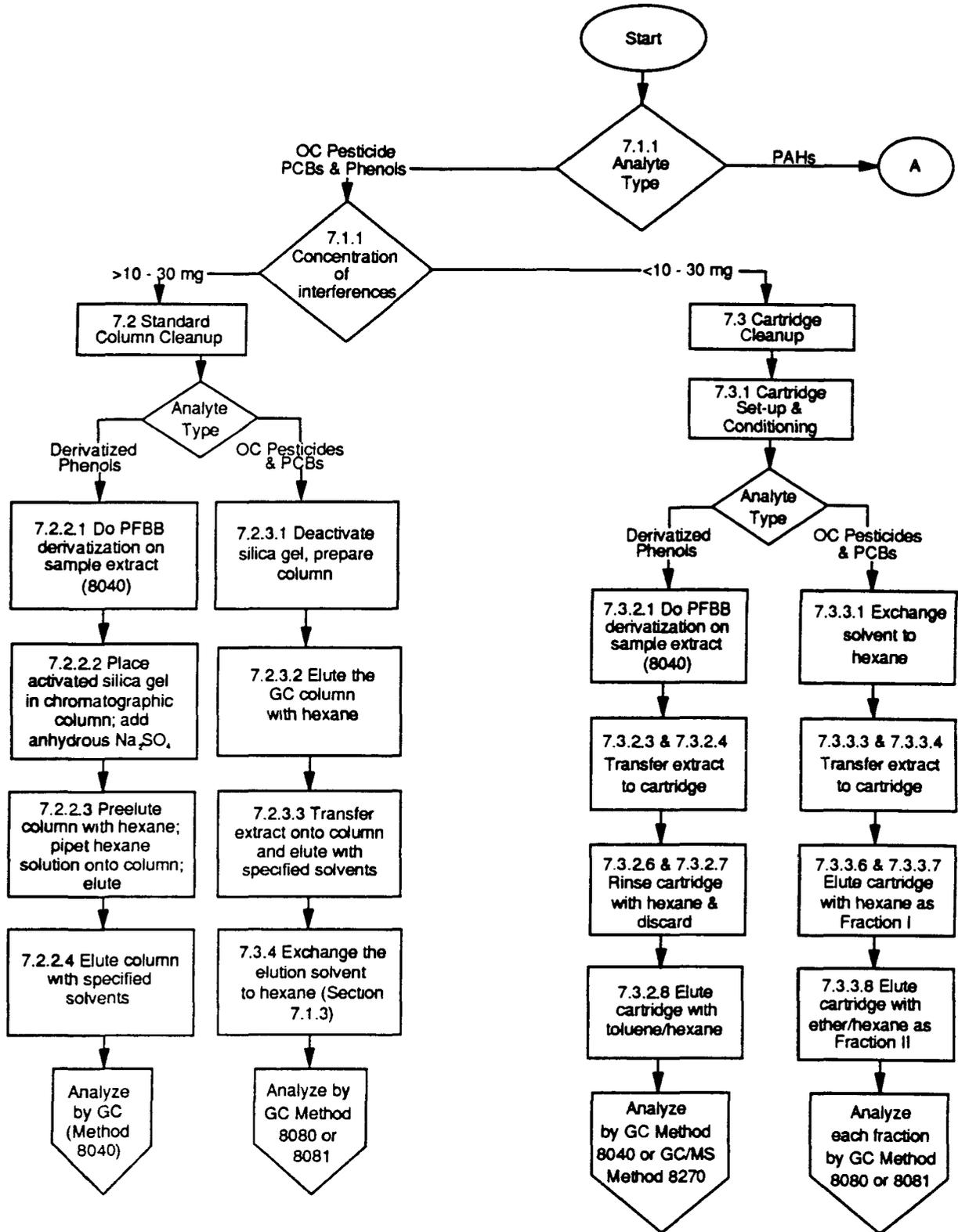
TABLE 4
 PERCENT RECOVERIES AND ELUTION PATTERNS FOR 17
 ORGANOCHLORINE PESTICIDES FROM 1 g SILICA CARTRIDGES^a

Compound	Fraction 1		Fraction 2	
	Average Recovery	Percent RSD	Average Recovery	Percent RSD
alpha-BHC	0		98.7	2.3
gamma-BHC	0		94.8	1.9
beta-BHC	0		94.3	3.0
Heptachlor	97.3	1.3	0	
delta-BHC	0		90.8	2.5
Aldrin	95.9	1.0	0	
Heptachlor epoxide	0		97.9	2.1
Endosulfan I	0		102	2.3
4,4'-DDE	99.9	1.7	0	
Dieldrin	0		92.3	2.0
Endrin	0		117	2.6
4,4'-DDD	10.7	41	92.4	3.3
Endosulfan II	0		96.0	2.2
4,4'-DDT	94.1	2.0	0	
Endrin aldehyde	0		59.7	2.6
Endosulfan sulfate	0		97.8	2.1
4,4'-Methoxychlor	0		98.0	2.4
Aroclor 1016	124			
Aroclor 1221	93.5			
Aroclor 1232	118			
Aroclor 1242	116			
Aroclor 1248	114			
Aroclor 1254	108			
Aroclor 1264	112			

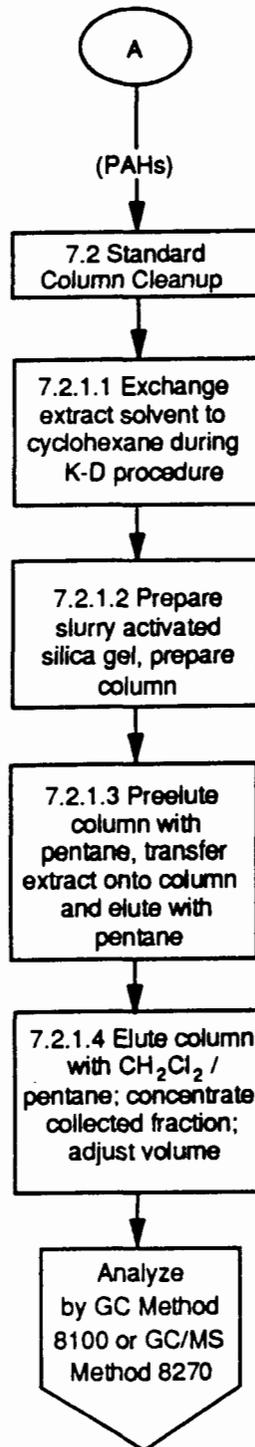
^a Silica cartridges (Supelco, Inc. lot SP0161) were used; each cartridge was conditioned with 4 mL hexane prior to use. The organochlorine pesticides were tested separately from PCBs. Each organochlorine pesticides experiment was performed in duplicate, at three spiking concentrations (0.2 µg, 1.0 µg, and 2.0 µg per compound per cartridge). Fraction 1 was eluted with 5 mL of hexane, Fraction 2 with 5 mL of diethyl ether/hexane (50/50, v/v). PCBs were spiked at 10 µg per cartridge and were eluted with 3 mL of hexane. The value given for PCBs is the percent recovery for a single determination.

Data from Reference 2

METHOD 3630B
SILICA GEL CLEANUP



METHOD 3630B
(continued)



METHOD 3640A

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion cleanup procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (1). The packing gel is porous and is characterized by the range or uniformity (exclusion range) of that pore size. In the choice of gels, the exclusion range must be larger than the molecular size of the molecules to be separated (2). A cross linked divinylbenzene-styrene copolymer (SX-3 Bio Beads or equivalent) is specified for this method.

1.2 General cleanup application - GPC is recommended for the elimination from the sample of lipids, polymers, copolymers, proteins, natural resins and polymers, cellular components, viruses, steroids, and dispersed high-molecular-weight compounds (2). GPC is appropriate for both polar and non-polar analytes, therefore, it can be effectively used to cleanup extracts containing a broad range of analytes.

1.3 Specific application - This method includes guidance for cleanup of sample extracts containing the following analytes from the RCRA Appendix VIII and Appendix IX lists:

Compound Name	CAS No. ^a
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Acetophenone	98-86-2
2-Acetylaminofluorene	53-96-3
Aldrin	309-00-2
4-Aminobiphenyl	92-67-1
Aniline	62-53-3
Anthracene	120-12-7
Benomyl	17804-35-2
Benzenethiol	108-98-5
Benzidine	92-87-5
Benz(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzo(k)fluoranthene	207-08-9
Benzoic acid	65-85-0
Benzotrichloride	98-07-7
Benzyl alcohol	100-51-6
Benzyl chloride	100-44-7
alpha-BHC	319-84-6
beta-BHC	319-85-7
gamma-BHC	58-89-9

Compound Name	CAS No. ^a
delta-BHC	319-86-8
4-Bromophenyl phenyl ether	101-55-3
Butyl benzyl phthalate	85-68-7
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	88-85-7
Carbazole	86-74-8
Carbendazim	10605-21-7
alpha-Chlordane	5103-71-9
gamma-Chlordane	5566-34-7
4-Chloro-3-methylphenol	59-50-7
4-Chloroaniline	106-47-8
Chlorobenzilate	510-15-6
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-chloroethyl) ether	111-44-4
Bis(2-chloroisopropyl) ether	108-60-1
2-Chloronaphthalene	91-58-7
2-Chlorophenol	95-57-8
4-Chlorophenol	106-48-9
3-Chlorophenol	108-43-0
4-Chlorophenyl phenyl ether	7005-72-3
3-Chloropropionitrile	542-76-7
Chrysene	218-01-9
2-Cresol	95-48-7
3-Cresol	108-39-4
4-Cresol	106-44-5
Cyclophosphamide	50-18-0
DDD	72-54-8
DDE	72-55-9
DDT	50-29-3
Di-n-butyl phthalate	84-74-2
Diallate	2303-16-4
Dibenzo(a,e)pyrene	192-65-4
Dibenzo(a,i)pyrene	189-55-9
Dibenz(a,j)acridine	224-42-0
Dibenz(a,h)anthracene	53-70-3
Dibenzofuran	132-64-9
Dibenzothiophene	132-65-0
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
trans-1,4-Dichloro-2-butene	110-57-6
cis-1,4-Dichloro-2-butene	1476-11-5
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	106-46-7
1,4-Dichlorobenzene	541-73-1
3,3'-Dichlorobenzidine	91-94-1
2,6-Dichlorophenol	87-65-0
2,4-Dichlorophenoxyacetic acid (2,4-D)	94-75-7
2,4-Dichlorophenol	120-83-2
2,4-Dichlorotoluene	95-73-8
1,3-Dichloro-2-propanol	96-23-1

Compound Name

CAS No.^a

Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethoate	60-51-5
Dimethyl phthalate	131-11-3
p-Dimethylaminoazobenzene	60-11-7
7,12-Dimethyl-benz(a)anthracene	57-97-6
2,4-Dimethylphenol	105-67-9
3,3-Dimethylbenzidine	119-93-7
4,6-Dinitro-o-cresol	534-52-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrophenol	51-28-5
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
Diphenylamine	122-39-4
Diphenyl ether	101-84-8
1,2-Diphenylhydrazine	122-66-7
Disulfoton	298-04-4
Endosulfan sulfate	1031-07-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Endrin ketone	53494-70-5
Ethyl methane sulfonate	62-50-0
Ethyl methacrylate	97-63-2
Bis(2-ethylhexyl) phthalate	117-81-7
Famphur	52-85-7
Fluorene	86-73-7
Fluoranthene	206-44-0
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocyclopentadiene	77-47-4
Hexachloroethane	67-72-1
Hexachloropropene	1888-71-7
Indeno(1,2,3-cd)pyrene	193-39-5
Isodrin	465-73-6
Isophorone	78-59-1
cis-Isosafrole	17627-76-8
trans-Isosafrole	4043-71-4
Kepone	143-50-0
Malononitrile	109-77-3
Merphos	150-50-5
Methoxychlor	72-43-5
3-Methylcholanthrene	56-49-5
2-Methylnaphthalene	91-57-6
Methyl parathion	298-00-0
4,4'-Methylene-bis(2-chloroaniline)	101-14-4

Compound Name	CAS No. ^a
Naphthalene	91-20-3
1,4-Naphthoquinone	130-15-4
2-Naphthylamine	91-59-8
1-Naphthylamine	134-32-7
5-Nitro-o-toluidine	99-55-8
2-Nitroaniline	88-74-4
3-Nitroaniline	99-09-2
4-Nitroaniline	100-01-6
Nitrobenzene	98-95-3
2-Nitrophenol	79-46-9
4-Nitrophenol	100-02-7
N-Nitrosodi-n-butylamine	924-16-3
N-Nitrosodiethanolamine	1116-54-7
N-Nitrosodiethylamine	55-18-5
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
N-Nitrosomethylethylamine	10595-95-6
N-Nitrosomorpholine	59-89-2
N-Nitrosopiperidine	100-75-4
N-Nitrosopyrrolidine	930-55-2
Di-n-octyl phthalate	117-84-0
Parathion	56-38-2
Pentachlorobenzene	608-93-5
Pentachloroethane	76-01-7
Pentachloronitrobenzene (PCNB)	82-68-8
Pentachlorophenol	87-86-5
Phenacetin	62-44-2
Phenanthrene	85-01-8
Phenol	108-95-2
1,2-Phenylenediamine	95-54-5
Phorate	298-02-2
2-Picoline	109-06-8
Pronamide	23950-58-5
Pyrene	129-00-0
Resorcinol	108-46-3
Safrole	94-59-7
1,2,4,5-Tetrachlorobenzene	95-94-3
2,3,5,6-Tetrachloronitrobenzene	117-18-0
2,3,5,6-Tetrachlorophenol	935-95-5
2,3,4,6-Tetrachlorophenol	58-90-2
Tetraethyl dithiopyrophosphate (Sulfotep)	3689-24-5
Thiosemicarbazide	79-19-6
2-Toluidine	106-49-0
4-Toluidine	95-53-4
Thiourea, 1-(o-chlorophenyl)	5344-82-1
Toluene-2,4-diamine	95-80-7
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1

Compound Name	CAS No. ^a
2,4,6-Trichlorophenol	88-06-2
2,4,5-Trichlorophenol	95-95-4
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	93-76-5
2,4,5-Trichlorophenoxypropionic acid (2,4,5-TP)	93-72-1
Warfarin	81-81-2

^a Chemical Abstract Services Registry Number.

Table 1 presents average percent recovery and percent RSD data for these analytes, as well as the retention volumes of each analyte on a single GPC system. Retention volumes vary from column to column. Figure 1 provides additional information on retention volumes for certain classes of compounds. The data for the semivolatiles was determined by GC/MS, whereas, the pesticide data was determined by GC/ECD or GC/FPD. Compounds not amenable to GC were determined by HPLC. Other analytes may also be appropriate for this cleanup technique, however, recovery through the GPC should be >70%.

1.4 Normally, this method is most efficient for removing high boiling materials that condense in the injection port area of a gas chromatograph (GC) or the front of the GC column. This residue will ultimately reduce the chromatographic separation efficiency or column capacity because of adsorption of the target analytes on the active sites. Pentachlorophenol is especially susceptible to this problem. GPC, operating on the principal of size exclusion, will not usually remove interference peaks that appear in the chromatogram since the molecular size of these compounds is relative similar to the target analytes. Separation cleanup techniques, based on other molecular characteristics (i.e., polarity), must be used to eliminate this type of interference.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required amount of preswelled absorbent, and is flushed with solvent for an extended period. The column is calibrated and then loaded with the sample extract to be cleaned up. Elution is effected with a suitable solvent(s) and the product is then concentrated.

3.0 INTERFERENCES

3.1 A reagent blank should be analyzed for the compound of interest prior to the use of this method. The level of interferences must be below the estimated quantitation limits (EQLs) of the analytes of interest before this method is performed on actual samples.

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

4.0 APPARATUS

4.1 Gel-permeation chromatography system - GPC Autoprep Model 1002 A or B, or equivalent, Analytical Biochemical Laboratories, Inc. Systems that perform very satisfactorily have also been assembled from the following components - an HPLC pump, an auto sampler or a valving system with sample loops, and a fraction collector. All systems, whether automated or manual, must meet the calibration requirements of Section 7.2.2.

4.1.1 Chromatographic column - 700 mm x 25 mm ID glass column. Flow is upward. (Optional) To simplify switching from the UV detector during calibration to the GPC collection device during extract cleanup, attach a double 3-way valve (Rheodyne Type 50 Teflon Rotary Valve #10-262 or equivalent) so that the column exit flow can be shunted either to the UV flow-through cell or to the GPC collection device.

4.1.2 Guard column - (Optional) 5 cm, with appropriate fittings to connect to the inlet side of the analytical column (Supelco 5-8319 or equivalent).

4.1.3 Bio Beads (S-X3) - 200-400 mesh, 70 gm (Bio-Rad Laboratories, Richmond, CA, Catalog 152-2750 or equivalent). An additional 5 gm of Bio Beads is required if the optional guard column is employed. The quality of Bio Beads may vary from lot to lot because of excessive fines in some lots. The UV chromatogram of the Calibration solution should be very similar to that in Figure 2, and the backpressure should be within 6-10 psi. Also, the gel swell ratio in methylene chloride should be in the range of 4.4 - 4.8 mL/gm. In addition to fines having a detrimental effect on chromatography, they can also pass through the column screens and damage the valve.

4.1.4 Ultraviolet detector - Fixed wavelength (254 nm) with a semi-prep flow-through cell.

4.1.5 Strip chart recorder, recording integrator or laboratory data system.

4.1.6 Syringe - 10 mL with Luerlok fitting.

4.1.7 Syringe filter assembly, disposable - Bio-Rad "Prep Disc" sample filter assembly #343-0005, 25 mm, and 5 micron filter discs or equivalent. Check each batch for contaminants. Rinse each filter assembly (prior to use) with methylene chloride if necessary.

4.2 Analytical balance - 0.0001 g.

4.3 Volumetric flasks, Class A - 10 mL to 1000 mL

4.4 Graduated cylinders

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2 . Pesticide quality or equivalent.

5.1.1 Some brands of methylene chloride may contain unacceptably high levels of acid (HCl). Check the pH by shaking equal portions of methylene chloride and water, then check the pH of the water layer.

5.1.1.1 If the pH of the water layer is ≤ 5 , filter the entire supply of solvent through a 2 in. x 15 in. glass column containing activated basic alumina. This column should be sufficient for processing approximately 20-30 liters of solvent. Alternatively, a different supply of methylene chloride should be found.

5.2 Cyclohexane, C_6H_{12} . Pesticide quality or equivalent.

5.3 n-Butyl chloride, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$. Pesticide quality or equivalent.

5.4 GPC Calibration Solution. Prepare a calibration solution in methylene chloride containing the following analytes (in elution order):

<u>Compound</u>	<u>mg/L</u>
corn oil	25,000
bis(2-ethylhexyl) phthalate	1000
methoxychlor	200
perylene	20
sulfur	80

NOTE: Sulfur is not very soluble in methylene chloride, however, it is soluble in warm corn oil. Therefore, one approach is to weigh out the corn oil, warm it and transfer the weighed amount of sulfur into the warm corn oil. Mix it and then transfer into a volumetric flask with methylene chloride, along with the other calibration compounds.

Store the calibration solution in an amber glass bottle with a Teflon lined screw-cap at 4°C , and protect from light. (Refrigeration may cause the corn oil to precipitate. Before use, allow the calibration solution to stand at room temperature until the corn oil dissolves.) Replace the calibration standard solution every 6 months, or more frequently if necessary.

5.5 Corn Oil Spike for Gravimetric Screen. Prepare a solution of corn oil in methylene chloride (5 mg/100 μL).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 It is very important to have consistent laboratory temperatures during an entire GPC run, which could be 24 hours or more. If temperatures are not consistent, retention times will shift, and the dump and collect times determined by the calibration standard will no longer be appropriate. The ideal laboratory temperature to prevent outgassing of the methylene chloride is 72°F.

7.2 GPC Setup and Calibration

7.2.1 Column Preparation

7.2.1.1 Weigh out 70 gm of Bio Beads (SX-3). Transfer them to a quart bottle with a Teflon lined cap or a 500 ml separatory funnel with a large bore stopcock, and add approximately 300 mL of methylene chloride. Swirl the container to ensure the wetting of all beads. Allow the beads to swell for a minimum of 2 hours. Maintain enough solvent to sufficiently cover the beads at all times. If a guard column is to be used, repeat the above with 5 gm of Bio Beads in a 125 mL bottle or a beaker, using 25 mL of methylene chloride.

7.2.1.2 Turn the column upside down from its normal position, and remove the inlet bed support plunger (the inlet plunger is longer than the outlet plunger). Position and tighten the outlet bed support plunger as near the end as possible, but no closer than 5 cm (measured from the gel packing to the collar).

7.2.1.3 Raise the end of the outlet tube to keep the solvent in the GPC column, or close the column outlet stopcock if one is attached. Place a small amount of solvent in the column to minimize the formation of air bubbles at the base of poured column packing.

7.2.1.4 Swirl the bead/solvent slurry to get a homogeneous mixture and, if the wetting was done in a quart bottle, quickly transfer it to a 500 mL separatory funnel with a large bore stopcock. Drain the excess methylene chloride directly into the waste beaker, and then start draining the slurry into the column by placing the separatory funnel tip against the column wall. This will help to minimize bubble formation. Swirl occasionally to keep the slurry homogeneous. Drain enough to fill the column. Place the tubing from the column outlet into a waste beaker below the column, open the stopcock (if attached) and allow the excess solvent to drain. Raise the tube to stop the flow and close the stopcock when the top of the gel begins to look dry. Add additional methylene chloride to just rewet the gel.

7.2.1.5 Wipe any remaining beads and solvent from the inner walls of the top of the column with a laboratory tissue. Loosen the seal slightly on the other plunger assembly (long plunger) and insert it into the column. Make the seal just tight enough so that any beads on the glass surface will be pushed forward, but loose enough so that the plunger can be pushed forward.

CAUTION: Do not tighten the seal if beads are between the seal and the glass surface because this can damage the seal and cause leakage.

7.2.1.6 Compress the column as much as possible without applying excessive force. Loosen the seal and gradually pull out the plunger. Rinse and wipe off the plunger. Slurry any remaining beads and transfer them into the column. Repeat Section 7.2.1.5 and reinsert the plunger. If the plunger cannot be inserted and pushed in without allowing beads to escape around the seal, continue compression of the beads without tightening the seal, and loosen and remove the plunger as described. Repeat this procedure until the plunger is successfully inserted.

7.2.1.7 Push the plunger until it meets the gel, then compress the column bed about four centimeters.

7.2.1.8 Pack the optional 5 cm column with approximately 5 gm of preswelled beads (different guard columns may require different amounts). Connect the guard column to the inlet of the analytical column.

7.2.1.9 Connect the column inlet to the solvent reservoir (reservoir should be placed higher than the top of the column) and place the column outlet tube in a waste container. Placing a restrictor in the outlet tube will force air out of the column more quickly. A restrictor can be made from a piece of capillary stainless steel tubing of 1/16" OD x 10/1000" ID x 2". Pump methylene chloride through the column at a rate of 5 mL/min for one hour.

7.2.1.10 After washing the column for at least one hour, connect the column outlet tube, without the restrictor, to the inlet side of the UV detector. Connect the system outlet to the outlet side of the UV detector. A restrictor (same size as in Section 7.2.1.9) in the outlet tube from the UV detector will prevent bubble formation which causes a noisy UV baseline. The restrictor will not effect flow rate. After pumping methylene chloride through the column for an additional 1-2 hours, adjust the inlet bed support plunger until approximately 6-10 psi backpressure is achieved. Push the plunger in to increase pressure or slowly pull outward to reduce pressure.

7.2.1.11 When the GPC column is not to be used for several days, connect the column outlet line to the column inlet to prevent column drying and/or channeling. If channeling occurs, the gel must be removed from the column, reswelled, and repoured as described above. If drying occurs, methylene chloride should be pumped through the column until the observed column pressure is constant and the column appears wet. Always recalibrate after column drying has occurred to verify retention volumes have not changed.

7.2.2 Calibration of the GPC Column

7.2.2.1 Using a 10 mL syringe, load sample loop #1 with calibration solution (Section 5.6). With the ABC automated system, the 5 mL sample loop requires a minimum of 8 mL of the calibration solution. Use a firm, continuous pressure to push the sample onto the loop. Switch the valve so that GPC flow is through the UV flow-through cell.

7.2.2.2 Inject the calibration solution and obtain a UV trace showing a discrete peak for each component. Adjust the detector and/or recorder sensitivity to produce a UV trace similar to Figure 2 that meets the following requirements. Differences between manufacturers' cell volumes and detector sensitivities may require a dilution of the calibration solution to achieve similar results. An analytical flow-through detector cell will require a much less concentrated solution than the semi-prep cell, and therefore the analytical cell is not acceptable for use.

7.2.2.3 Following are criteria for evaluating the UV chromatogram for column condition.

7.2.2.3.1 Peaks must be observed, and should be symmetrical, for all compounds in the calibration solution.

7.2.2.3.2 Corn oil and phthalate peaks must exhibit >85% resolution.

7.2.2.3.3 Phthalate and methoxychlor peaks must exhibit >85% resolution.

7.2.2.3.4 Methoxychlor and perylene peaks must exhibit >85% resolution.

7.2.2.3.5 Perylene and sulfur peaks must not be saturated and must exhibit >90% baseline resolution.

7.2.2.4 Calibration for Semivolatiles - Using the information from the UV trace, establish appropriate collect and dump time periods to ensure collection of all target analytes. Initiate column eluate collection just before elution of bis(2-ethylhexyl) phthalate and after the elution of the corn oil. Stop eluate collection shortly after the elution of perylene. Collection should be stopped before sulfur elutes. Use a "wash" time of 10 minutes after the elution of sulfur. Each laboratory is required to establish its specific time sequences. See Figure 2 for general guidance on retention time. Figure 1 illustrates retention volumes for different classes of compounds.

7.2.2.5 Calibration for Organochlorine Pesticides/PCBs - Determine the elution times for the phthalate, methoxychlor, perylene, and sulfur. Choose a dump time which removes >85% of the phthalate, but collects >95% of the methoxychlor. Stop collection after the elution of perylene, but before sulfur elutes.

7.2.2.6 Verify the flow rate by collecting column eluate for 10 minutes in a graduated cylinder and measure the volume, which should be 45-55 mL (4.5-5.5 mL/min). If the flow rate is outside of this range, corrective action must be taken, as described above. Once the flow rate is within the range of 4.5-5.5 mL/min, record the column pressure (should be 6-10 psi) and room temperature. Changes in pressure, solvent flow rate, and temperature conditions can affect analyte retention times, and must be monitored. If the flow rate and/or column pressure do not fall within the above ranges, a new column should be prepared. A UV trace that does not meet the criteria in Section 7.2.2.3 would also indicate that a new column should be prepared. It may be necessary to obtain a new lot of Bio Beads if the column fails all the criteria.

7.2.2.7 Reinject the calibration solution after appropriate collect and dump cycles have been set, and the solvent flow and column pressure have been established.

7.2.2.7.1 Measure and record the volume of collected GPC eluate in a graduated cylinder. The volume of GPC eluate collected for each sample extract processed may be used to indicate problems with the system during sample processing.

7.2.2.7.2 The retention times for bis(2-ethylhexyl) phthalate and perylene must not vary more than $\pm 5\%$ between calibrations. If the retention time shift is $>5\%$, take corrective action. Excessive retention time shifts are caused by:

7.2.2.7.2.1 Poor laboratory temperature control or system leaks.

7.2.2.7.2.2 An unstabilized column that requires pumping methylene chloride through it for several more hours or overnight.

7.2.2.7.2.3 Excessive laboratory temperatures, causing outgassing of the methylene chloride.

7.2.2.8 Analyze a GPC blank by loading 5 mL of methylene chloride into the GPC. Concentrate the methylene chloride that passes through the system during the collect cycle using a Kuderna-Danish (KD) evaporator. Analyze the concentrate by whatever detectors will be used for the analysis of future samples. Exchange the solvent if necessary. If the blank exceeds the estimated quantitation limit of the analytes, pump additional methylene chloride through the system for 1-2 hours. Analyze another GPC blank to ensure the system is sufficiently clean. Repeat the methylene chloride pumping if necessary.

7.3 Extract Preparation

7.3.1 Adjust the extract volume to 10.0 mL. The solvent extract must be primarily methylene chloride. All other solvents, e.g. 1:1

methylene chloride/acetone, must be concentrated to 1 mL (or as low as possible if a precipitate forms) and diluted to 10.0 mL with methylene chloride. Thoroughly mix the sample before proceeding.

7.3.2 Filter the extract through a 5 micron filter disc by attaching a syringe filter assembly containing the filter disc to a 10 mL syringe. Draw the sample extract through the filter assembly and into the 10 mL syringe. Disconnect the filter assembly before transferring the sample extract into a small glass container, e.g. a 15 mL culture tube with a Teflon lined screw cap. Alternatively, draw the extract into the syringe without the filter assembly. Attach the filter assembly and force the extract through the filter and into the glass container. The latter is the preferred technique for viscous extracts or extracts with a lot of solids. Particulate larger than 5 microns may scratch the valve, which may result in a system leak and cross-contamination of sample extracts in the sample loops. Repair of the damaged valve is quite expensive.

NOTE: Viscosity of a sample extract should not exceed the viscosity of 1:1 water/glycerol. Dilute samples that exceed this viscosity.

7.4 Screening the Extract

7.4.1 Screen the extract to determine the concentration of dissolved residue by evaporating a 100 μ L aliquot to dryness and weighing the residue. The concentration of dissolved residue loaded on the GPC column cannot exceed 0.500 g. Concentrations exceeding 0.500 g will very likely result in incomplete extract cleanup and contamination of the GPC switching valve (which results in cross-contamination of sample extracts).

7.4.1.1 Transfer 100 μ L of the filtered extract from Section 7.3.2 to a tared aluminum weighing dish.

7.4.1.2 A suggested evaporation technique is to use a heat lamp. Set up a 250 watt heat lamp in a hood so that it is 8 ± 0.5 cm from a surface covered with a clean sheet of aluminum foil. Surface temperature should be 80-100°C (check temperature by placing a thermometer on the foil and under the lamp). Place the weighing dish under the lamp using tongs. Allow it to stay under the lamp for 1 min. Transfer the weighing dish to an analytical balance or a micro balance and weigh to the nearest 0.1 mg. If the residue weight is less than 10 mg/100 μ L, then further weighings are not necessary. If the residue weight is greater than 10 mg/100 μ L, then determine if constant weight has been achieved by placing the weighing dish and residue back under the heat lamp for 2 or more additional 0.5 min. intervals. Reweigh after each interval. Constant weight is achieved when three weights agree within $\pm 10\%$.

7.4.1.3 Repeat the above residue analysis on a blank and a spike. Add 100 μ L of the same methylene chloride used for the sample extraction, to a weighing dish and determine residue as above. Add 100 μ L of a corn oil spike (5 mg/100 μ L) to another weighing dish and repeat the residue determination.

7.4.2 A residue weight of 10 mg/100 μ L of extract represents 500 mg in 5 mL of extract. Any sample extracts that exceed the 10 mg/100 μ L residue weight must be diluted so that the 5 mL loaded on the GPC column does not exceed 0.500 g. When making the dilution, keep in mind that a minimum volume of 8 mL is required when loading the ABC GPC unit. Following is a calculation that may be used to determine what dilution is necessary if the residue exceeds 10 mg.

$$\begin{array}{rcl} \text{Y mL taken} & = & 10 \text{ mL final} \\ \text{for dilution} & & \text{volume} \end{array} \times \frac{10 \text{ mg maximum}}{\text{X mg of residue}}$$

Example:

$$\begin{array}{rcl} \text{Y mL taken} & = & 10 \text{ mL final} \\ \text{for dilution} & & \text{volume} \end{array} \times \frac{10 \text{ mg maximum}}{15 \text{ mg of residue}}$$

$$\text{Y mL taken for dilution} = 6.7 \text{ mL}$$

Therefore, taking 6.7 mL of sample extract from Section 7.3.2, and diluting to 10 mL with methylene chloride, will result in 5 mL of diluted extract loaded on the GPC column that contains 0.500 g of residue.

NOTE: This dilution factor must be included in the final calculation of analyte concentrations. In the above example, the dilution factor is 1.5.

7.5 GPC Cleanup

7.5.1 Calibrate the GPC at least once per week following the procedure outlined in Sections 7.2.2 through 7.2.2.6. Ensure that UV trace requirements, flow rate and column pressure criteria are acceptable. Also, the retention time shift must be <5% when compared to retention times in the last calibration UV trace.

7.5.1.1 If these criteria are not met, try cleaning the column by loading one or more 5 mL portions of butyl chloride and running it through the column. Butyl chloride removes the discoloration and particulate that may have precipitated out of the methylene chloride extracts. If a guard column is being used, replace it with a new one. This may correct the problem. If column maintenance does not restore acceptable performance, the column must be repacked with new Bio Beads and calibrated.

7.5.2 Draw a minimum of 8 mL of extract (diluted, if necessary, and filtered) into a 10 mL syringe.

7.5.3 Attach the syringe to the turn lock on the injection port. Use firm, continuous pressure to push the sample onto the 5-mL sample loop. If the sample is difficult to load, some part of the system may be blocked. Take appropriate corrective action. If the back pressure is normal (6-10 psi), the blockage is probably in the valve. Blockage may be flushed out of the valve by reversing the inlet and outlet tubes and pumping solvent through the tubes. (This should be done before sample loading.)

NOTE: Approximately 2 mL of the extract remains in the lines between the injection port and the sample loop; excess sample also passes through the sample loop to waste.

7.5.4 After loading a loop, and before removing the syringe from the injection port, index the GPC to the next loop. This will prevent loss of sample caused by unequal pressure in the loops.

7.5.5 After loading each sample loop, wash the loading port with methylene chloride in a PTFE wash bottle to minimize cross-contamination. Inject approximately 10 mL of methylene chloride to rinse the common tubes.

7.5.6 After loading all the sample loops, index the GPC to the 00 position, switch to the "RUN" mode and start the automated sequence. Process each sample using the collect and dump cycle times established in Section 7.2.2.

7.5.7 Collect each sample in a 250 mL Erlenmeyer flask, covered with aluminum foil to reduce solvent evaporation, or directly into a Kuderna-Danish evaporator. Monitor sample volumes collected. Changes in sample volumes collected may indicate one or more of the following problems:

7.5.7.1 Change in solvent flow rate, caused by channeling in the column or changes in column pressure.

7.5.7.2 Increase in column operating pressure due to the absorption of particles or gel fines onto either the guard column or the analytical column gel, if a guard column is not used.

7.5.7.3 Leaks in the system or significant variances in room temperature.

7.6 Concentrate the extract by the standard K-D technique (see any of the extraction methods, Section 4.2 of this chapter). See the determinative methods (Chapter Four, Section 4.3) for the final volume.

7.7 It should be remembered that only half of the sample extract is processed by the GPC (5 mL of the 10 mL extract is loaded onto the GPC column), and thus, a dilution factor of 2 (or 2 multiplied by any dilution factor in Section 7.4.2) must be used for quantitation of the sample in the determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 3600 for specific quality control procedures.

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

8.3 For sample extracts that are cleaned up using this method, the associated quality control samples must also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for single laboratory performance data.

10.0 REFERENCES

1. Wise, R.H.; Bishop, D.F.; Williams, R.T.; Austern, B.M. "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges"; U.S. EPA Municipal Environmental Research Laboratory: Cincinnati, Ohio 45268.
2. Czuczwa, J.; Alford-Stevens, A. "Optimized Gel Permeation Chromatographic Cleanup for Soil, Sediment, Waste and Waste Oil Sample Extracts for GC/MS Determination of Semivolatile Organic Pollutants, JAOAC, submitted April 1989.
3. Marsden, P.J.; Taylor, V.; Kennedy, M.R. "Evaluation of Method 3640 Gel Permeation Cleanup"; Contract No. 68-03-3375, U.S. Environmental Protection Agency, Cincinnati, Ohio, pp. 100, 1987.

TABLE 1
GPC RECOVERY AND RETENTION VOLUMES FOR RCRA
APPENDIX VIII ANALYTES

Compound	% Rec ¹	% RSD ²	Ret. Vol. ³ (mL)
Acenaphthene	97	2	196-235
Acenaphthylene	72	10	196-235
Acetophenone	94	7	176-215
2-Acetylaminofluorene	97	2	156-195
Aldrin	99	9	196-215
4-Aminobiphenyl	96	7	176-215
Aniline	93	4	196-235
Anthracene	89	2	196-235
Benomyl	131	8	146-195
Benzenethiol	92	11	196-235
Benzidine	95	5	176-215
Benz(a)anthracene	100	3	196-235
Benzo(b)fluoranthene	93	5	196-235
Benzo(a)pyrene	93	3	196-235
Benzo(ghi)perylene	90	6	196-235
Benzo(k)fluoranthene	91	4	196-235
Benzoic acid	66	7	176-195
Benzotrichloride	93	7	176-215
Benzyl alcohol	95	17	176-215
Benzyl chloride	99	4	176-215
alpha-BHC	84	13	196-215
beta-BHC	94	9	196-215
gamma-BHC	93	4	196-215
delta-BHC	102	7	216-255
4-Bromophenyl phenyl ether	93	1	176-215
Butyl benzyl phthalate	104	3	136-175
2-sec-butyl-4,6-dinitrophenol (Dinoseb)	103	18	176-195
Carbazole	99	5	196-255
Carbendazim	131	8	146-195
alpha-Chlordane	97	2	196-235
gamma-Chlordane	93	2	196-215
4-Chloro-3-methylphenol	87	1	196-255
4-Chloroaniline	88	3	196-235
Chlorobenzilate	92	5	176-235
Bis(2-chloroethoxy)methane	89	1	156-195
Bis(2-chloroethyl) ether	76	2	156-215
Bis(2-chloroisopropyl) ether	83	2	156-195
2-Chloronaphthalene	89	1	196-235
2-Chlorophenol	90	1	196-215
3-Chlorophenol	86	3	196-215
4-Chlorophenol	87	2	196-215
4-Chlorophenyl phenyl ether	98	2	176-215
3-Chloropropionitrile	80	5	176-215
Chrysene	102	1	196-235
2-Cresol	91	1	196-215
3-Cresol	70	3	196-215

TABLE 1 (continued)

Compound	% Rec ¹	%RSD ²	Ret. Vol. ³ (mL)
4-Cresol	88	2	196-215
Cyclophosphamide	114	10	146-185
DDD	94	4	196-235
DDE	94	2	196-235
DDT	96	6	176-215
Di-n-butyl phthalate	104	3	136-175
Diallate	97	6	156-175
Dibenzo(a,e)pyrene	94	10	216-235
Dibenzo(a,i)pyrene	99	8	216-235
Dibenz(a,j)acridine	117	9	176-195
Dibenz(a,h)anthracene	92	5	196-235
Dibenzofuran	94	1	176-235
Dibenzothiophene	94	3	196-235
1,2-Dibromo-3-chloropropane	83	2	176-215
1,2-Dibromoethane	121	8	196-215
trans-1,4-Dichloro-2-butene	107	6	176-195
cis-1,4-Dichloro-2-butene	106	6	176-215
1,2-Dichlorobenzene	81	1	196-235
1,3-Dichlorobenzene	81	1	196-235
1,4-Dichlorobenzene	81	1	196-235
3,3'-Dichlorobenzidine	98	3	176-215
2,6-Dichlorophenol	86	3	196-215
2,4-Dichlorophenoxyacetic acid (2,4-D)	80	NA	76-215
2,4-Dichlorophenol	87	2	96-215
2,4-Dichlorotoluene	70	9	196-235
1,3-Dichloro-2-propanol	73	13	176-215
Dieldrin	100	5	196-215
Diethyl phthalate	103	3	136-195
Dimethoate	79	15	146-185
3,3'-Dimethoxybenzidine ^a	15	11	156-195
Dimethyl phthalate	100	1	156-195
p-Dimethylaminoazobenzene	96	1	176-215
7,12-Dimethyl-benz(a)anthracene	77	1	176-215
2,4-Dimethylphenol	93	2	176-215
3,3'-Dimethylbenzidine	93	2	156-215
4,6-Dinitro-o-cresol	100	1	156-195
1,3-Dinitrobenzene	99	2	156-195
2,4-Dinitrophenol	118	7	176-195
2,4-Dinitrotoluene	93	4	156-195
2,6-Dinitrotoluene	101	2	156-175
Diphenylamine	95	6	176-235
Diphenyl ether	67	12	196-215
1,2-Diphenylhydrazine	92	1	176-215
Disulfoton	81	15	146-165
Endosulfan sulfate	94	2	176-195
Endosulfan I	99	8	176-215
Endosulfan II	92	6	196-215
Endrin	95	6	196-215

TABLE 1 (continued)

Compound	% Rec ¹	%RSD ²	Ret. Vol. ³ (mL)
Endrin aldehyde	97	1	176-215
Endrin ketone	94	4	176-215
Ethyl methane sulfonate	62	7	176-235
Ethyl methacrylate	126	7	176-195
Bis(2-ethylhexyl) phthalate	101	1	120-145
Famphur	99	NA	126-165
Fluorene	95	1	176-235
Fluoranthene	94	1	196-235
Heptachlor	85	2	195-215
Heptachlor epoxide	91	11	156-195
Hexachlorobenzene	108	2	196-235
Hexachlorobutadiene	86	2	176-215
Hexachlorocyclopentadiene	89	3	176-215
Hexachloroethane	85	1	196-235
Hexachloropropene	91	2	196-235
Indeno(1,2,3-cd)pyrene	79	13	216-255
Isodrin	98	5	196-235
Isophorone	68	7	156-195
cis-Isosafrole	90	4	176-215
trans-Isosafrole	88	16	156-195
Kepone	102	NA	196-235
Malononitrile	111	9	156-195
Merphos	93	12	126-165
Methoxychlor	94	6	156-195
3-Methylcholanthrene	74	12	176-195
2-Methylnaphthalene	67	6	196-215
Methyl parathion	84	13	146-185
4,4'-Methylene-bis(2-chloroaniline)	96	1	176-215
Naphthalene	95	7	196-215
1,4-Naphthoquinone	73	7	176-215
2-Naphthylamine	94	8	196-235
1-Naphthylamine	96	6	196-235
5-Nitro-o-toluidine	77	2	176-195
2-Nitroaniline	96	8	176-215
3-Nitroaniline	96	2	176-215
4-Nitroaniline	103	8	176-215
Nitrobenzene	86	2	176-195
2-Nitrophenol	95	3	176-195
4-Nitrophenol	77	3	196-215
N-Nitroso-di-n-butylamine	89	4	156-175
N-Nitrosodiethanolamine	104	3	146-185
N-Nitrosodiethylamine	94	2	156-175
N-Nitrosodimethylamine	86	13	156-195
N-Nitrosodiphenylamine	99	2	156-195
N-Nitrosodi-n-propylamine	85	4	156-175
N-Nitrosomethylethylamine	83	7	156-175
N-Nitrosomorpholine	86	4	156-195
N-Nitrosopiperidine	84	4	156-195

TABLE 1 (continued)

Compound	% Rec ¹	%RSD ²	Ret. Vol. ³ (mL)
N-Nitrosopyrrolidine	92	1	156-175
Di-n-octyl phthalate	83	4	120-156
Parathion	109	14	146-170
Pentachlorobenzene	95	2	196-235
Pentachloroethane	74	1	196-235
Pentachloronitrobenzene (PCNB)	91	8	156-195
Pentachlorophenol	102	1	196-215
Phenacetin	100	3	156-195
Phenanthrene	94	2	196-235
Phenol	83	2	156-195
1,2-Phenylenediamine	91	1	196-215
Phorate	74	NA	116-135
2-Picoline	99	14	156-215
Pronamide	105	15	156-195
Pyrene	98	2	215-235
Resorcinol	70	6	196-215
Safrole	93	1	176-215
Streptozotocin ^a	6	48	225-245
1,2,4,5-Tetrachlorobenzene	96	2	196-235
2,3,5,6-Tetrachloro-nitrobenzene	85	9	176-215
2,3,4,6-Tetrachlorophenol	95	1	196-215
2,3,5,6-Tetrachlorophenol	96	7	196-215
Tetraethyl dithiopyrophosphate (Sulfotep)	89	14	116-135
Thiosemicarbazide	74	3	146-185
2-Toluidine	92	3	176-235
4-Toluidine	87	8	176-235
Thiourea, 1-(o-chlorophenyl)	75	11	166-185
Toluene-2,4-diamine	69	7	176-215
1,2,3-Trichlorobenzene	87	1	196-235
1,2,4-Trichlorobenzene	89	1	196-235
2,4,5-Trichlorophenol	77	1	216-235
2,4,6-Trichlorophenol	95	1	216-235
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	71	23	156-235
2,4,5-Trichlorophenoxypropionic acid	67	NA	216-215
Warfarin	94	2	166-185

NA = Not applicable, recovery presented as the average of two determinations.

^a Not an appropriate analyte for this method.

¹ The percent recovery is based on an average of three recovery values.

² The % relative standard deviation is determined from three recovery values.

³ These Retention Volumes are for guidance only as they will differ from column to column and from system to system.

Figure 1
GPC RETENTION VOLUME OF CLASSES OF ANALYTES

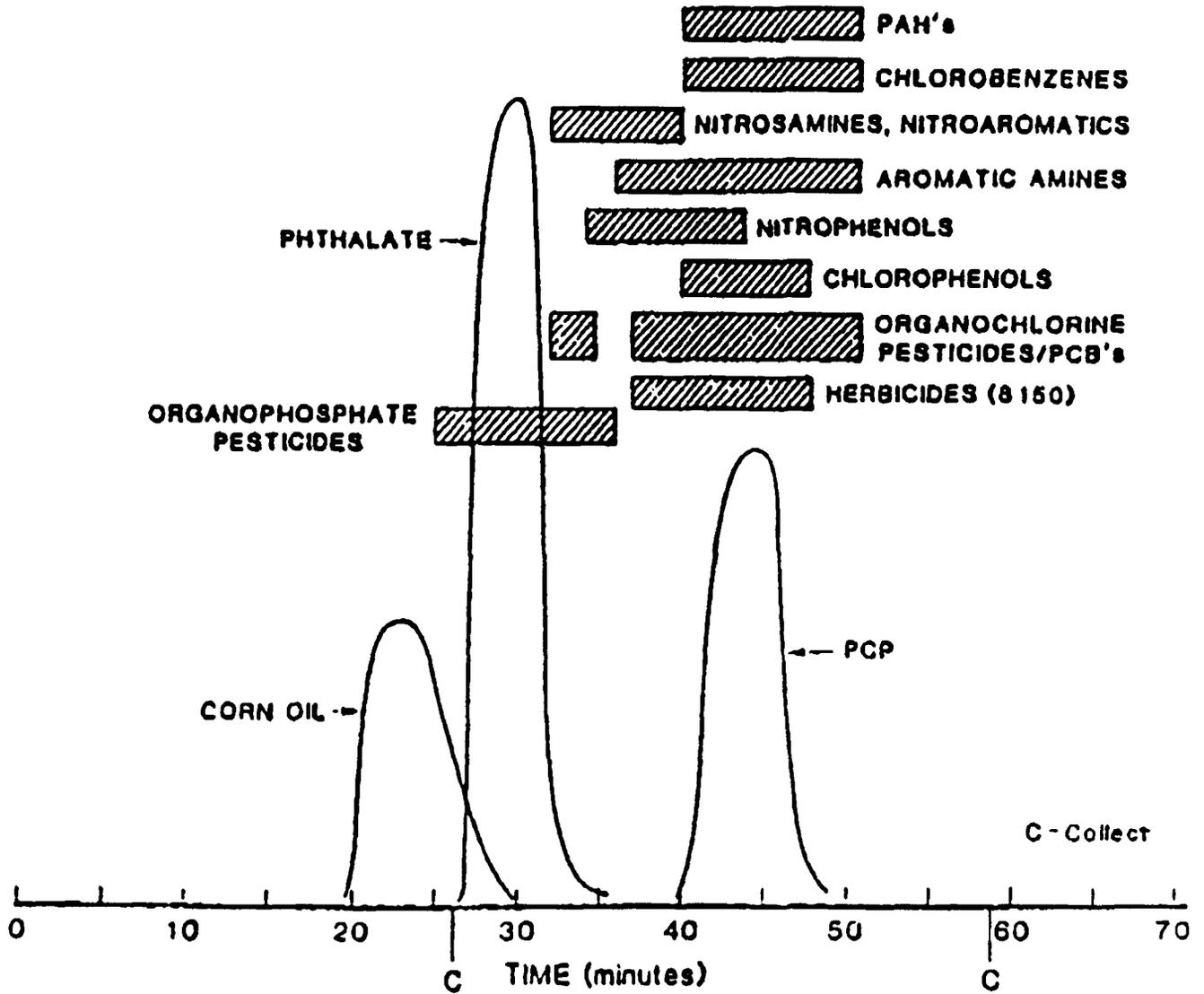
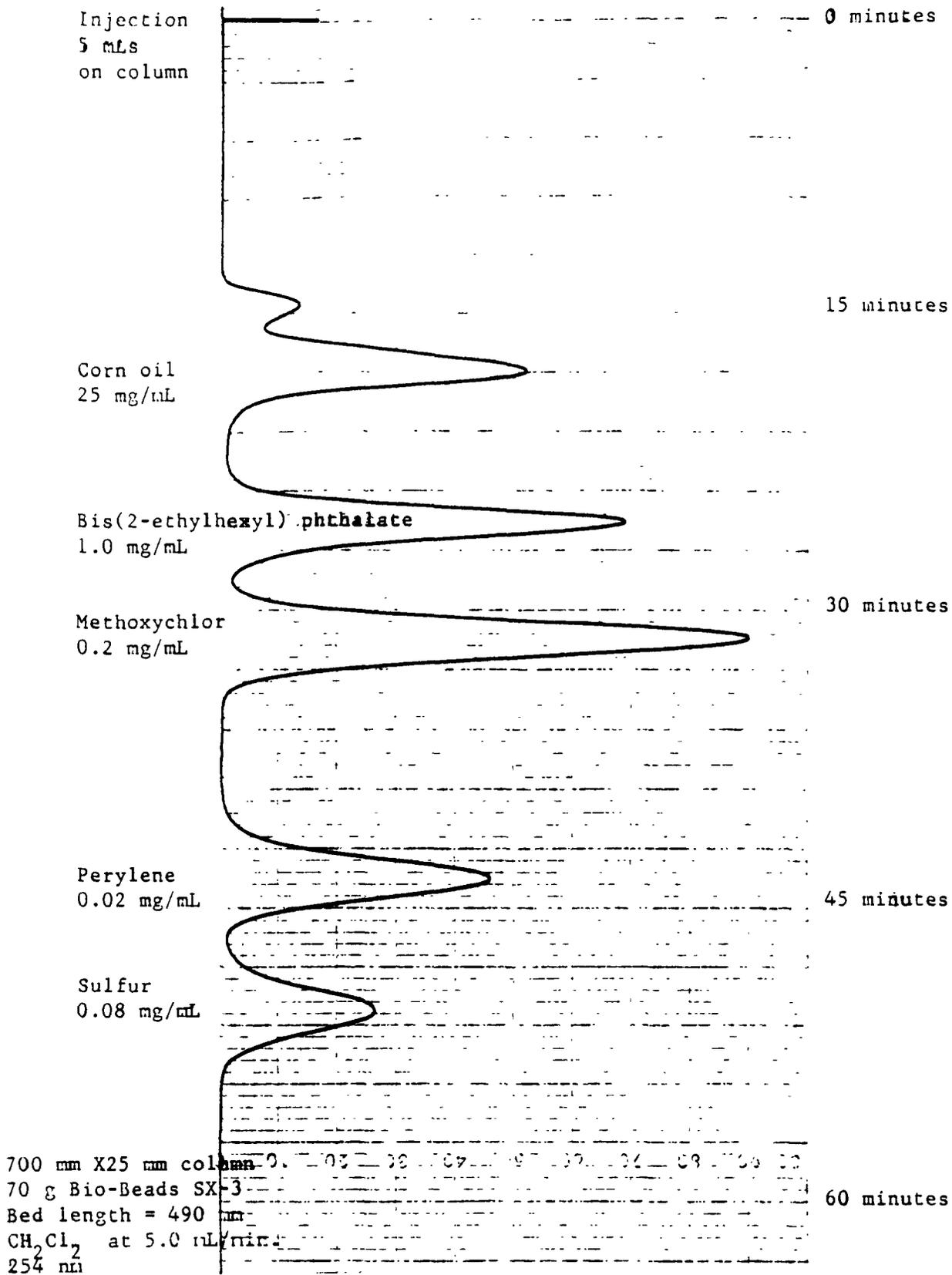
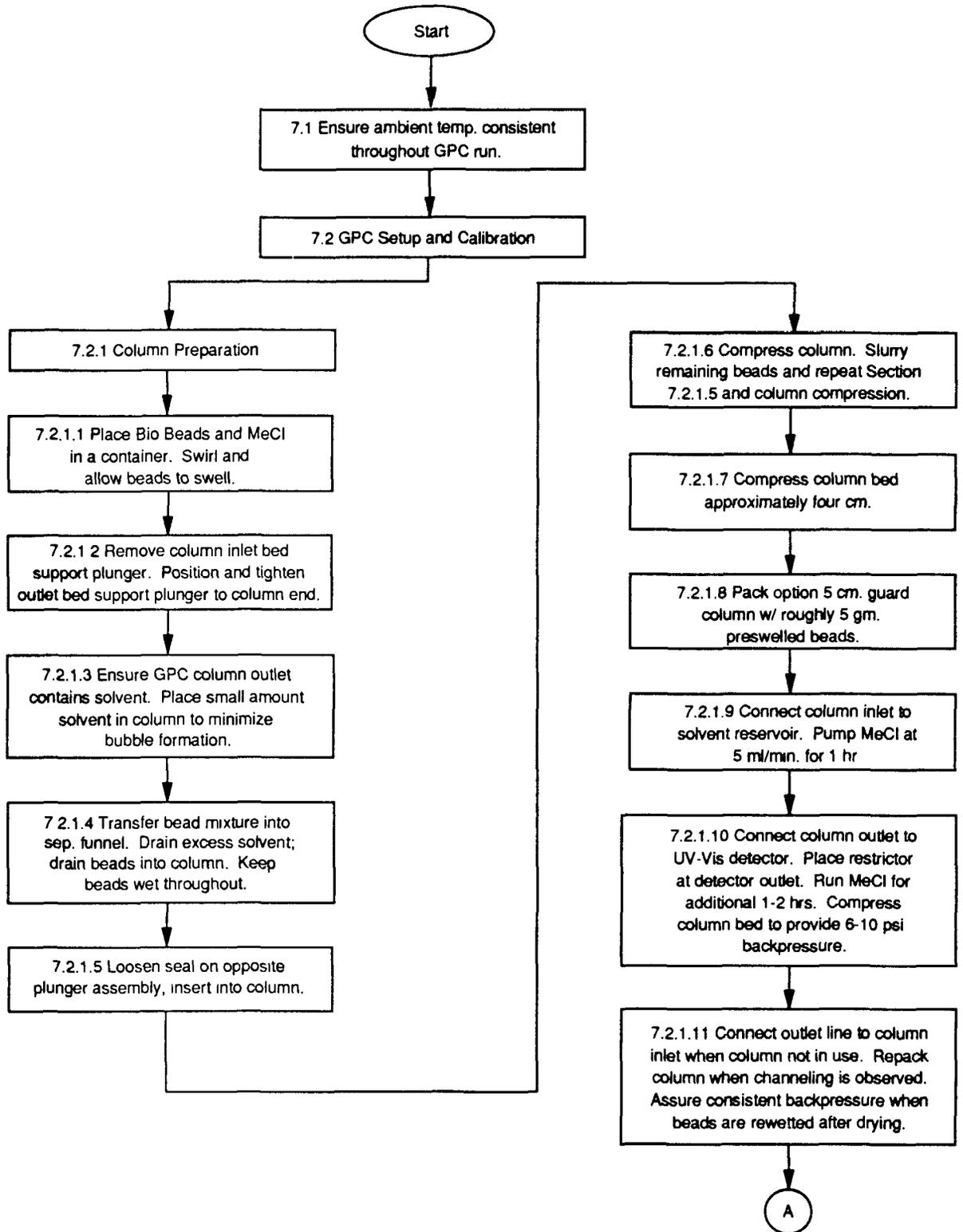


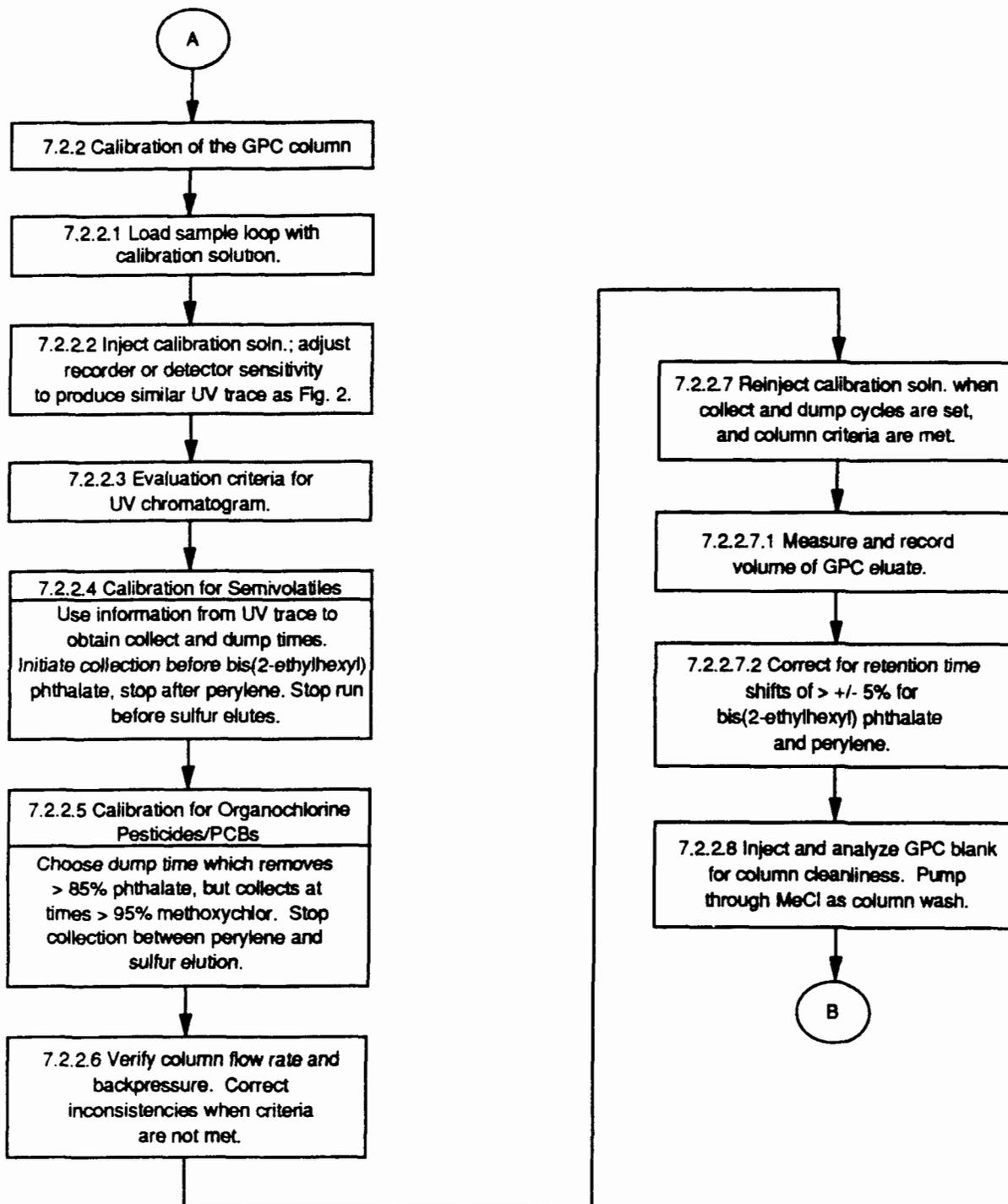
Figure 2
 UV CHROMATOGRAM OF THE CALIBRATION SOLUTION



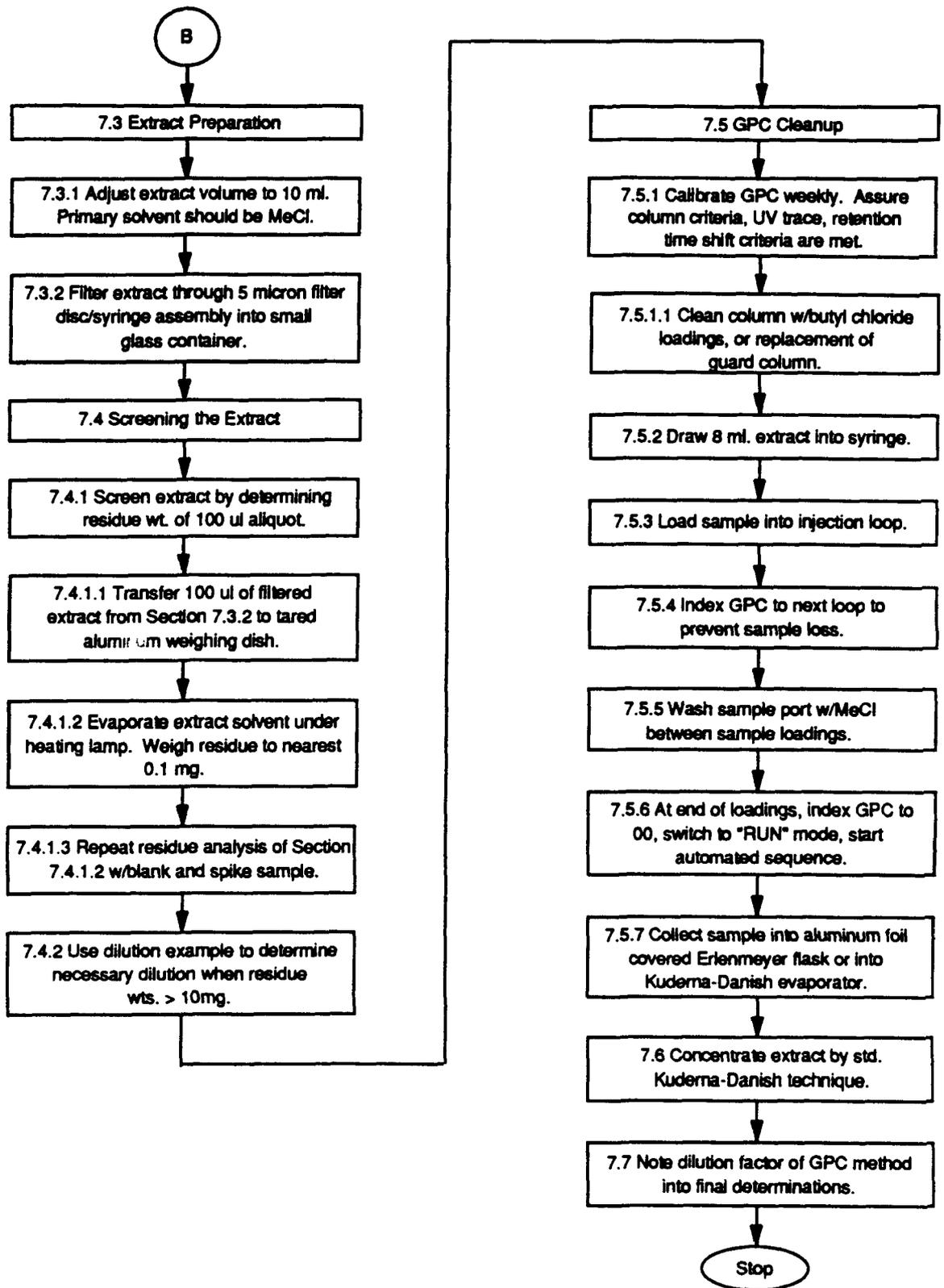
METHOD 3640A
GEL-PERMEATION CLEANUP



METHOD 3640A
continued



METHOD 3640A
continued



METHOD 3665

SULFURIC ACID/PERMANGANATE CLEANUP

1.0 SCOPE AND APPLICATION

1.1 This method is suitable for the rigorous cleanup of sample extracts prior to analysis for polychlorinated biphenyls. This method should be used whenever elevated baselines or overly complex chromatograms prevent accurate quantitation of PCBs. This method cannot be used to cleanup extracts for other target analytes, as it will destroy most organic chemicals including the pesticides Aldrin, Dieldrin, Endrin, Endosulfan (I and II), and Endosulfan sulfate.

2.0 SUMMARY OF METHOD

2.1 An extract is solvent exchanged to hexane, then the hexane is sequentially treated with (1) concentrated sulfuric acid and (2) 5% aqueous potassium permanganate. Appropriate caution must be taken with these corrosive reagents.

2.2 Blanks and replicate analysis samples must be subjected to the same cleanup as the samples associated with them.

2.3 It is important that all the extracts be exchanged to hexane before initiating the following treatments.

3.0 INTERFERENCES

3.1 This technique will not destroy chlorinated benzenes, chlorinated naphthalenes (Halowaxes), and a number of chlorinated pesticides.

4.0 APPARATUS

4.1 Syringe or Class A volumetric pipet, glass; 1.0, 2.0 and 5.0 mL.

4.2 Vials - 1, 2 and 10 mL, glass with Teflon lined screw caps or crimp tops.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Vortex mixer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sulfuric acid/Water, H_2SO_4/H_2O , (1:1, v/v).

5.4 Hexane, C_6H_{14} - Pesticide grade or equivalent.

5.5 Potassium permanganate, $KMnO_4$, 5 percent aqueous solution (w/v).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sulfuric acid cleanup

7.1.1 Using a syringe or a volumetric pipet, transfer 1.0 or 2.0 mL of the hexane extract to a 10 mL vial and, in a fume hood, carefully add 5 mL of the 1:1 sulfuric acid/water solution.

7.1.2 The volume of hexane extract used depends on the requirements of the GC autosampler used by the laboratory. If the autosampler functions reliably with 1 mL of sample volume, 1.0 mL of extract should be used. If the autosampler requires more than 1 mL of sample volume, 2.0 mL of extract should be used.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.1.3 Cap the vial tightly and vortex for one minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks, AVOID SKIN CONTACT, SULFURIC ACID BURNS.

7.1.4 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer; it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.1.5 If a clean phase separation is achieved, proceed to Section 7.1.8.

7.1.6 If the hexane layer is colored or the emulsion persists for several minutes, remove the sulfuric acid layer from the vial and dispose of it properly. Add another 5 mL of the clean 1:1 sulfuric acid/water.

NOTE: Do not remove any hexane at this stage of the procedure.

7.1.7 Vortex the sample for one minute and allow the phases to separate.

7.1.8 Transfer the hexane layer to a clean 10 mL vial.

7.1.9 Add an additional 1 mL of hexane to the sulfuric acid layer, cap and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.1.10 Remove the second hexane layer and combine with the hexane from Section 7.1.8.

7.2 Permanganate cleanup

7.2.1 Add 5 mL of the 5 percent aqueous potassium permanganate solution to the combined hexane fractions from 7.1.10.

CAUTION: Make sure that there is no exothermic reaction nor evolution of gas prior to proceeding.

7.2.2 Cap the vial tightly and vortex for 1 minute. A vortex must be visible in the vial.

CAUTION: Stop the vortexing immediately if the vial leaks. AVOID SKIN CONTACT, POTASSIUM PERMANGANATE BURNS.

7.2.3 Allow the phases to separate for at least 1 minute. Examine the top (hexane) layer, it should not be highly colored nor should it have a visible emulsion or cloudiness.

7.2.4 If a clean phase separation is achieved, proceed to Section 7.2.7.

7.2.5 If the hexane layer is colored or the emulsion persists for several minutes, remove the permanganate solution from the vial via a

glass pipette and dispose of it properly. Add another 5 mL of the clean aqueous permanganate solution.

NOTE: Do not remove any hexane at this stage of the procedure.

7.2.6 Vortex the sample and allow the phases to separate.

7.2.7 Transfer the hexane layer to a clean 10 mL vial.

7.2.8 Add an additional 1 mL of hexane to the permanganate layer, cap the vial securely and shake. This second extraction is done to ensure quantitative transfer of the PCBs and Toxaphene.

7.2.9 Remove the second hexane layer and combine with the hexane from Section 7.2.7.

7.3 Final preparation

7.3.1 Reduce the volume of the combined hexane layers to the original volume (1 or 2 mL) using the Kuderna-Danish Technique (Section 7.3.1.1).

7.3.1.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of hexane to the top of the column. Place the K-D apparatus on a hot water bath (15-20°C above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-20 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 from the water bath and allow it to drain and cool for at least 10 minutes.

7.3.1.2 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of hexane. The extract may be further concentrated by using either the micro Snyder column technique (Section 7.3.2) or nitrogen blowdown technique (Section 7.3.3).

7.3.2 Micro Snyder Column Technique

7.3.2.1 Add another one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of hexane to the top of the column. Place the K-D apparatus in a hot water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 5-10 minutes. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water

bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with about 0.2 mL of hexane and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL, as required, with hexane.

7.3.3 Nitrogen Blowdown Technique

7.3.3.1 Place the concentrator tube in a warm water bath (approximately 35°C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.3.3.2 The internal wall of the tube must be rinsed down several times with the appropriate solvent during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.3.4 Remove any remaining organochlorine pesticides from the extracts using Florisil Column Cleanup (Method 3620) or Silica Gel Cleanup (Method 3630).

7.3.5 The extracts obtained may now be analyzed for the target analytes using the appropriate organic technique(s) (see Section 4.3 of this Chapter). If analysis of the extract will not be performed immediately, stopper the concentrator tube and store in a refrigerator. If the extract will be stored longer than 2 days, it should be transferred to a vial with a Teflon lined screw cap or crimp top, and labeled appropriately.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

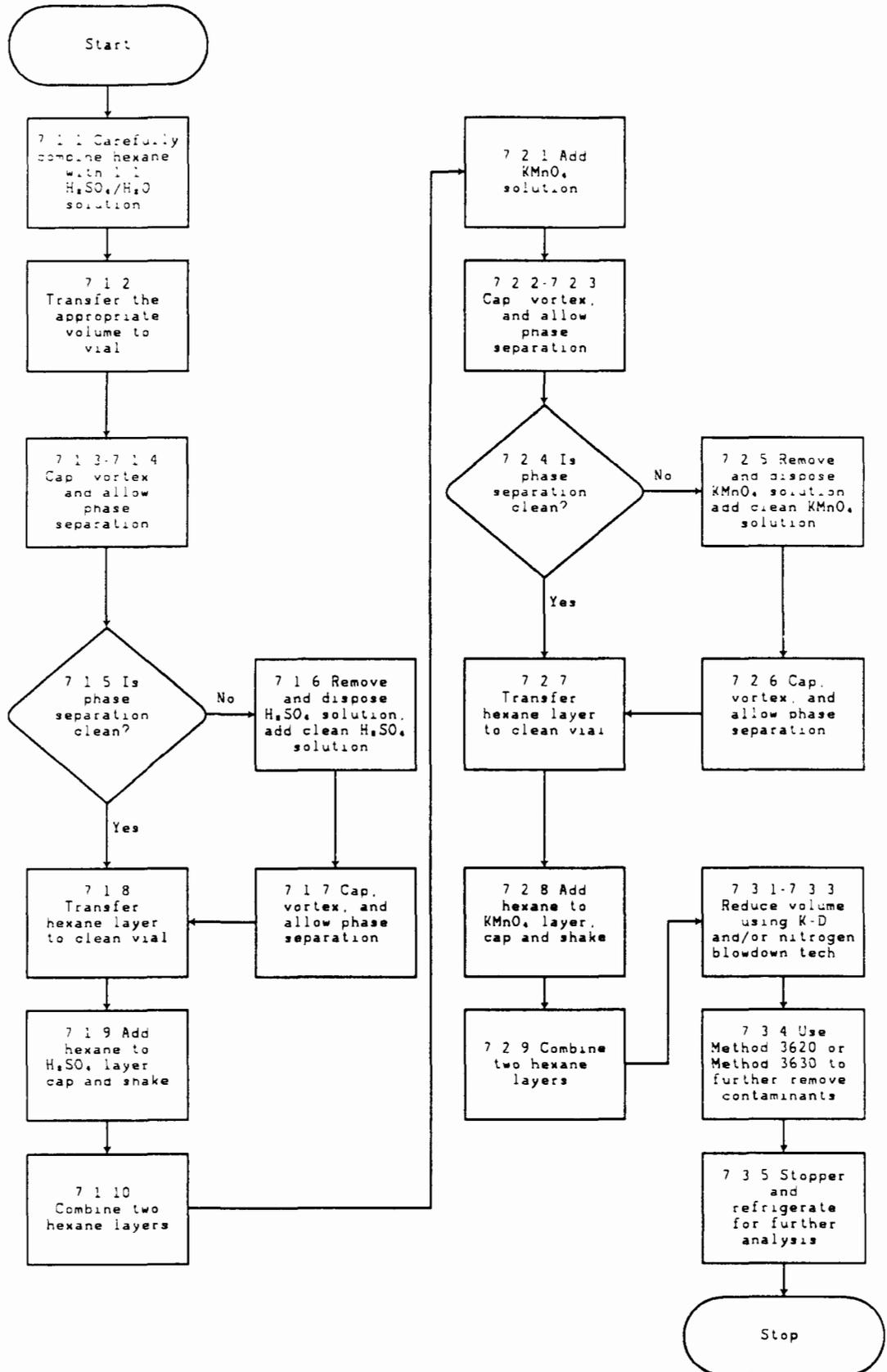
9.0 METHOD PERFORMANCE

9.1 No performance data are currently available.

10.0 REFERENCES

None required.

METHOD 3665
SULFURIC ACID/PERMANGANATE CLEANUP



METHOD 8000

GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Gas chromatography is a quantitative analytical technique useful for organic compounds capable of being volatilized without being decomposed or chemically rearranged. Gas chromatography (GC), also known as vapor phase chromatography (VPC), has two subcategories distinguished by: gas-solid chromatography (GSC), and gas-liquid chromatography (GLC) or gas-liquid partition chromatography (GLPC). This last group is the most commonly used, distinguished by type of column adsorbent or packing.

1.2 The gas chromatographic methods are recommended for use only by, or under the close supervision of, experienced residue analysts.

2.0 SUMMARY OF METHOD

2.1 Each organic analytical method that follows provides a recommended technique for extraction, cleanup, and occasionally, derivatization of the samples to be analyzed. Before the prepared sample is introduced into the GC, a procedure for standardization must be followed to determine the recovery and the limits of detection for the analytes of interest. Following sample introduction into the GC, analysis proceeds with a comparison of sample values with standard values. Quantitative analysis is achieved through integration of peak area or measurement of peak height.

3.0 INTERFERENCES

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak areas is recommended.

4.2 Gas chromatographic columns - See the specific determinative method. Other packed or capillary (open-tubular) columns may be used if the requirements of Step 8.6 are met.

5.0 REAGENTS

5.1 See the specific determinative method for the reagents needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Extraction - Adhere to those procedures specified in the referring determinative method.

7.2 Cleanup and separation - Adhere to those procedures specified in the referring determinative method.

7.3 The recommended gas chromatographic columns and operating conditions for the instrument are specified in the referring determinative method.

7.4 Calibration

7.4.1 Establish gas chromatographic operating parameters equivalent to those indicated in Section 7.0 of the determinative method of interest. Prepare calibration standards using the procedures indicated in Section 5.0 of the determinative method of interest. Calibrate the chromatographic system using either the external standard technique (Step 7.4.2) or the internal standard technique (Step 7.4.3).

7.4.2 External standard calibration procedure

7.4.2.1 For each analyte of interest, prepare calibration standards at a minimum of five concentration levels by adding volumes of one or more stock standards to a volumetric flask and diluting to volume with an appropriate solvent. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.2.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph (e.g. 2-5- μ L injections, purge-and-trap, etc.). Tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for each analyte. Alternatively, for samples that are introduced into the gas chromatograph using a syringe, the ratio of the response to the amount injected, defined as the calibration factor (CF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the calibration factor is less than 20% over the working range, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve.

$$\text{Calibration factor} = \frac{\text{Total Area of Peak}^*}{\text{Mass injected (in nanograms)}}$$

*For multiresponse pesticides/PCBs use the total area of all peaks used for quantitation.

7.4.2.3 The working calibration curve or calibration factor must be verified on each working day by the injection of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_1} \times 100$$

where:

R_1 = Calibration Factor from first analysis.

R_2 = Calibration Factor from succeeding analyses.

7.4.3 Internal standard calibration procedure

7.4.3.1 To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.4.3.2 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest by adding volumes of one or more stock standards to a volumetric flask. To each calibration standard, add a known constant amount of one or more internal standards and dilute to volume with an appropriate solvent. One of the standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the detector.

7.4.3.3 Inject each calibration standard using the same introduction technique that will be applied to the actual samples (e.g. 2- to 5-uL injection, purge-and-trap, etc.). Tabulate the peak height or area responses against the concentration of each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_S C_{iS}) / (A_{iS} C_S)$$

where:

A_S = Response for the analyte to be measured.

A_{iS} = Response for the internal standard.

C_{iS} = Concentration of the internal standard, ug/L.

C_S = Concentration of the analyte to be measured, ug/L.

If the RF value over the working range is constant (< 20% RSD), the RF can be assumed to be invariant, and the average RF can be used for calculations. Alternatively, the results can be used to plot a calibration curve of response ratios, A_S/A_{iS} versus RF.

7.4.3.4 The working calibration curve or RF must be verified on each working day by the measurement of one or more calibration standards. The frequency of verification is dependent on the detector. Detectors, such as the electron capture detector, that operate in the sub-nanogram range are more susceptible to changes in detector response caused by GC column and sample effects. Therefore, more frequent verification of calibration is necessary. The flame ionization detector is much less sensitive and requires less frequent verification. If the response for any analyte varies from the predicted response by more than $\pm 15\%$, a new calibration curve must be prepared for that compound.

7.5 Retention time windows

7.5.1 Before establishing windows, make sure the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures and multiresponse products (i.e. PCBs) throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in retention time windows that are too tight.

7.5.2 Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one major peak from the envelope and calculate the standard deviation of the three retention times for that peak. The peak chosen should be fairly immune to losses due to degradation and weathering in samples.

7.5.2.1 Plus or minus three times the standard deviation of the absolute retention times for each standard will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse products (i.e. PCBs), the analyst should use the retention time window but should primarily rely on pattern recognition.

7.5.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

7.5.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.6 Gas chromatographic analysis

7.6.1 Introduction of organic compounds into the gas chromatograph varies depending on the volatility of the compound. Volatile organics are primarily introduced by purge-and-trap (Method 5030). However, there are limited applications where direct injection is acceptable. Use of Method 3810 or 3820 as a screening technique for volatile organic analysis may be valuable with some sample matrices to prevent overloading and contamination of the GC systems. Semivolatile organics are introduced by direct injection.

7.6.2 The appropriate detector(s) is given in the specific method.

7.6.3 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

7.6.4 Direct Injection - 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 or peak height.

7.6.5 If the responses exceed the linear range of the system, dilute the extract and reanalyze. It is recommended that extracts be diluted so that all peaks are on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration.

7.6.6 If peak detection is prevented by the presence of interferences, further cleanup is required.

7.6.7 Examples of chromatograms for the compounds of interest are frequently available in the referring analytical method.

7.6.8 Calibrate the system immediately prior to conducting any analyses (see Step 7.4). A midlevel standard must also be injected at intervals specified in the method and at the end of the analysis sequence. The calibration factor for each analyte to be quantitated, must not exceed a 15% difference when compared to the initial standard of

the analysis sequence. When this criteria is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary (see Step 7.7) before recalibrating and proceeding with sample analysis. All samples that were injected after the sample exceeding the criteria must be reinjected.

7.6.9 Establish daily retention time windows for each analyte. Use the absolute retention time for each analyte from Step 7.6.8 as the midpoint of the window for that day. The daily retention time window equals the midpoint \pm three times the standard deviation determined in Step 7.5.

7.6.9.1 Tentative identification of an analyte occurs when a peak from a sample extract falls within the daily retention time window. Normally, confirmation is required: on a second GC column, by GC/MS if concentration permits, or by other recognized confirmation techniques. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

7.6.9.2 Validation of GC system qualitative performance: Use the midlevel standards interspersed throughout the analysis sequence (Step 7.6.8) to evaluate this criterion. If any of the standards fall outside their daily retention time window, the system is out of control. Determine the cause of the problem and correct it (see Step 7.7).

7.7 Suggested chromatography system maintenance - Corrective measures may require any one or more of the following remedial actions.

7.7.1 Packed columns - For instruments with injection port traps, replace the demister trap, clean, and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Inspect the injection end of the column and remove any foreign material (broken glass from the rim of the column or pieces of septa). Replace the glass wool with fresh deactivated glass wool. Also, it may be necessary to remove the first few millimeters of the packing material if any discoloration is noted, also swab out the inside walls of the column if any residue is noted. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body (described in Step 7.7.3) and/or repack/replace the column.

7.7.2 Capillary columns - Clean and deactivate the glass injection port insert or replace with a cleaned and deactivated insert. Break off the first few inches, up to one foot, of the injection port side of the column. Remove the column and solvent backflush according to the manufacturer's instructions. If these procedures fail to eliminate the degradation problem, it may be necessary to deactivate the metal injector body and/or replace the column.

7.7.3 Metal injector body - Turn off the oven and remove the analytical column when the oven has cooled. Remove the glass injection port insert (instruments with off-column injection or Grob). Lower the

injection port temperature to room temperature. Inspect the injection port and remove any noticeable foreign material.

7.7.3.1 Place a beaker beneath the injector port inside the GC oven. Using a wash bottle, serially rinse the entire inside of the injector port with acetone and then toluene; catching the rinsate in the beaker.

7.7.3.2 Prepare a solution of deactivating agent (Sylon-CT or equivalent) following manufacturer's directions. After all metal surfaces inside the injector body have been thoroughly coated with the deactivation solution, serially rinse the injector body with toluene, methanol, acetone, and hexane. Reassemble the injector and replace the GC column.

7.8 Calculations

7.8.1 External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of standard purged or injected, from the peak response, using the calibration curve or the calibration factor determined in Step 7.4.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples

$$\text{Concentration (ug/L)} = [(A_X)(A)(V_t)(D)]/[(A_S)(V_i)(V_S)]$$

where:

A_X = Response for the analyte in the sample, units may be in area counts or peak height.

A = Amount of standard injected or purged, ng.

A_S = Response for the external standard, units same as for A_X .

V_i = Volume of extract injected, uL. For purge-and-trap analysis, V_i is not applicable and therefore = 1.

D = Dilution factor, if dilution was made on the sample prior to analysis. If no dilution was made, $D = 1$, dimensionless.

V_t = Volume of total extract, uL. For purge-and-trap analysis, V_t is not applicable and therefore = 1.

V_S = Volume of sample extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration (ng/g)} = [(A_X)(A)(V_t)(D)]/[(A_S)(V_i)(W)]$$

where:

W = Weight of sample extracted or purged, g. The wet weight or dry weight may be used, depending upon the specific applications of the data.

A_x , A_s , A, V_t , D, and V_i have the same definition as for aqueous samples.

7.8.2 Internal standard calibration - For each analyte of interest, the concentration of that analyte in the sample is calculated as follows:

Aqueous samples

$$\text{Concentration (ug/L)} = [(A_x)(C_{is})(D)]/[(A_{is})(RF)(V_s)]$$

where:

A_x = Response of the analyte being measured, units may be in area counts or peak height.

C_{is} = Amount of internal standard added to extract or volume purged, ng.

D = Dilution factor, if a dilution was made on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

A_{is} = Response of the internal standard, units same as A_x .

RF = Response factor for analyte, as determined in Step 7.4.3.3.

V_s = Volume of water extracted or purged, mL.

Nonaqueous samples

$$\text{Concentration (ug/kg)} = [(A_s)(C_{is})(D)]/[(A_{is})(RF)(W_s)]$$

where:

W_s = Weight of sample extracted, g. Either a dry weight or wet weight may be used, depending upon the specific application of the data.

A_s , C_{is} , D, A_{is} , and RF have the same definition as for aqueous samples.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses these methods is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document quality data. The laboratory must maintain records to document the quality of the data

generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

8.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

8.3 For each analytical batch (up to 20 samples), a reagent blank, matrix spike, and replicate or matrix spike replicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

8.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal?; Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

8.5 Required instrument QC

8.5.1 Step 7.4 requires that the %RSD vary by $< 20\%$ when comparing calibration factors to determine if a five point calibration curve is linear.

8.5.2 Step 7.4 sets a limit of $\pm 15\%$ difference when comparing daily response of a given analyte versus the initial response. If the limit is exceeded, a new standard curve must be prepared.

8.5.3 Step 7.5 requires the establishment of retention time windows.

8.5.4 Step 7.6.8 sets a limit of $\pm 15\%$ difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Step 7.6.9.2 requires that all succeeding standards in an analysis sequence must fall within the daily retention time window established by the first standard of the sequence.

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

8.6.1 A quality (QC) check sample concentrate is required containing each analyte of interest. The QC check sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC check sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.6.1.1 The concentration of the QC check sample concentrate is highly dependent upon the analytes being investigated. Therefore, refer to Method 3500, Section 8.0 for the required concentration of the QC check sample concentrate.

8.6.2 Preparation of QC check samples

8.6.2.1 Volatile organic analytes (Methods 8010, 8020, and 8030) - The QC check sample is prepared by adding 200 μ L of the QC check sample concentrate (Step 8.6.1) to 100 mL of water.

8.6.2.2 Semivolatile organic analytes (Methods 8040, 8060, 8080, 8090, 8100, and 8120) - The QC check sample is prepared by adding 1.0 mL of the QC check sample concentrate (Step 8.6.1) to each of four 1-L aliquots of water.

8.6.3 Four aliquots of the well-mixed QC check sample are analyzed by the same procedures used to analyze actual samples (Section 7.0 of each of the methods). For volatile organics, the preparation/analysis process is purge-and-trap/gas chromatography. For semivolatile organics, the QC check samples must undergo solvent extraction (see Method 3500) prior to chromatographic analysis.

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

8.6.5 For each analyte compare s and \bar{x} with the corresponding acceptance criteria for precision and accuracy, respectively, given the QC Acceptance Criteria Table at the end of each of the determinative methods. If s and \bar{x} for all analytes of interest meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If any individual s exceeds the precision limit or any individual \bar{x} falls outside the range for accuracy, then the system performance is unacceptable for that analyte.

NOTE: The large number of analytes in each of the QC Acceptance Criteria Tables present a substantial probability that one or more will fail at least one of the acceptance criteria when all analytes of a given method are determined.

8.6.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.6.6.1 or 8.6.6.2.

8.6.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Step 8.6.2.

8.6.6.2 Beginning with Step 8.6.2, repeat the test only for those analytes that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Step 8.6.2.

8.7 The laboratory must, on an ongoing basis, analyze a reagent blank and a matrix spiked replicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of spiked replicates. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

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

8.7.1.1 If, as in compliance monitoring, the concentration of a specific analyte in the sample is being checked against a regulatory concentration limit, the spike should be at that limit or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in a water sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC reference sample (Step 8.6.2) or 1 to 5 times higher than the background concentration determined in Step 8.7.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 20 times the PQL.

8.7.1.3 For semivolatile organics, it may not be possible to determine the background concentration levels prior to spiking (e.g. maximum holding times will be exceeded). If this is the case, the spike concentration should be (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or the QC reference sample concentration (Step 8.6.2). For other matrices, the recommended spiking concentration is 20 times the PQL.

8.7.2 Analyze one unspiked and one spiked sample aliquot to determine percent recovery of each of the spiked compounds.

8.7.2.1 Volatile organics - Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1)

appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as $100(A - B)/T$, where T is the known true value of the spike.

8.7.2.2 Semivolatiles organics - Analyze one sample aliquot (extract of 1-L sample) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC reference sample concentrate (Step 8.6.1) appropriate for the background concentration in the sample. Spike a second 1-L sample aliquot with 1.0 mL of the QC reference sample concentrate and analyze it to determine the concentration after spiking (A) of each analyte. Calculate each percent recovery (p) as $100(A - B)/T$, where T is the known true value of the spike.

8.7.3 Compare the percent recovery (p) for each analyte in a water sample with the corresponding criteria presented in the QC Acceptance Criteria Table found at the end of each of the determinative methods. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than the QC reference sample concentration (Step 8.6.2), the analyst must use either the QC acceptance criteria presented in the Tables, or optional QC acceptance criteria calculated for the specific spike concentration. To calculate optional acceptance criteria for the recovery of an analyte: (1) Calculate accuracy (x') using the equation found in the Method Accuracy and Precision as a Function of Concentration Table (appears at the end of each determinative method), substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in the same Table, substituting x' for x ; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.7.4 If any individual p falls outside the designated range for recovery, that analyte has failed the acceptance criteria. A check standard containing each analyte that failed the criteria must be analyzed as described in Step 8.8.

8.8 If any analyte in a water sample fails the acceptance criteria for recovery in Step 8.7, a QC reference standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC reference standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes given in a method must be measured in the sample in Step 8.7, the probability that the analysis of a QC check standard will be required is high. In this case the QC check standard should be routinely analyzed with the spiked sample.

8.8.1 Preparation of the QC check sample - For volatile organics, add 10 uL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 5 mL of water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Step 8.6.1 or 8.7.2) to 1 L of water. The QC check sample needs only to contain the analytes that failed criteria in the test in Step 8.7. Prepare the QC check sample for analysis following the guidelines given in Method 3500 (e.g. purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check sample to determine the concentration measured (A) of each analyte. Calculate each percent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

8.8.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in the appropriate Table in each of the methods. Only analytes that failed the test in Step 8.7 need to be compared with these criteria. If the recovery of any such analyte falls outside the designated range, the laboratory performance for that analyte is judged to be out of control, and the problem must be immediately identified and corrected. The result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.9 As part of the QC program for the laboratory, method accuracy for each matrix studied must be assessed and records must be maintained. After the analysis of five spiked samples (of the same matrix type) as in Step 8.7, calculate the average percent recovery (\bar{p}) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $\bar{p} - 2s_p$ to $\bar{p} + 2s_p$. If $\bar{p} = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.10 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.10.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.10.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (\bar{p}) and standard deviation of the percent recovery (s) for each of the surrogates.

8.10.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

$$\begin{aligned}\text{Upper Control Limit (UCL)} &= \bar{p} + 3s \\ \text{Lower Control Limit (LCL)} &= \bar{p} - 3s\end{aligned}$$

8.10.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Tables A and B of Methods 8240 and 8270,

respectively. The limits given in these methods are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.10.3 must fall within those given in Tables A and B for these matrices.

8.10.5 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.10.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.11 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column, specific element detector, or mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in the referring analytical methods were obtained using water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 Refer to the determinative method for specific method performance information.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

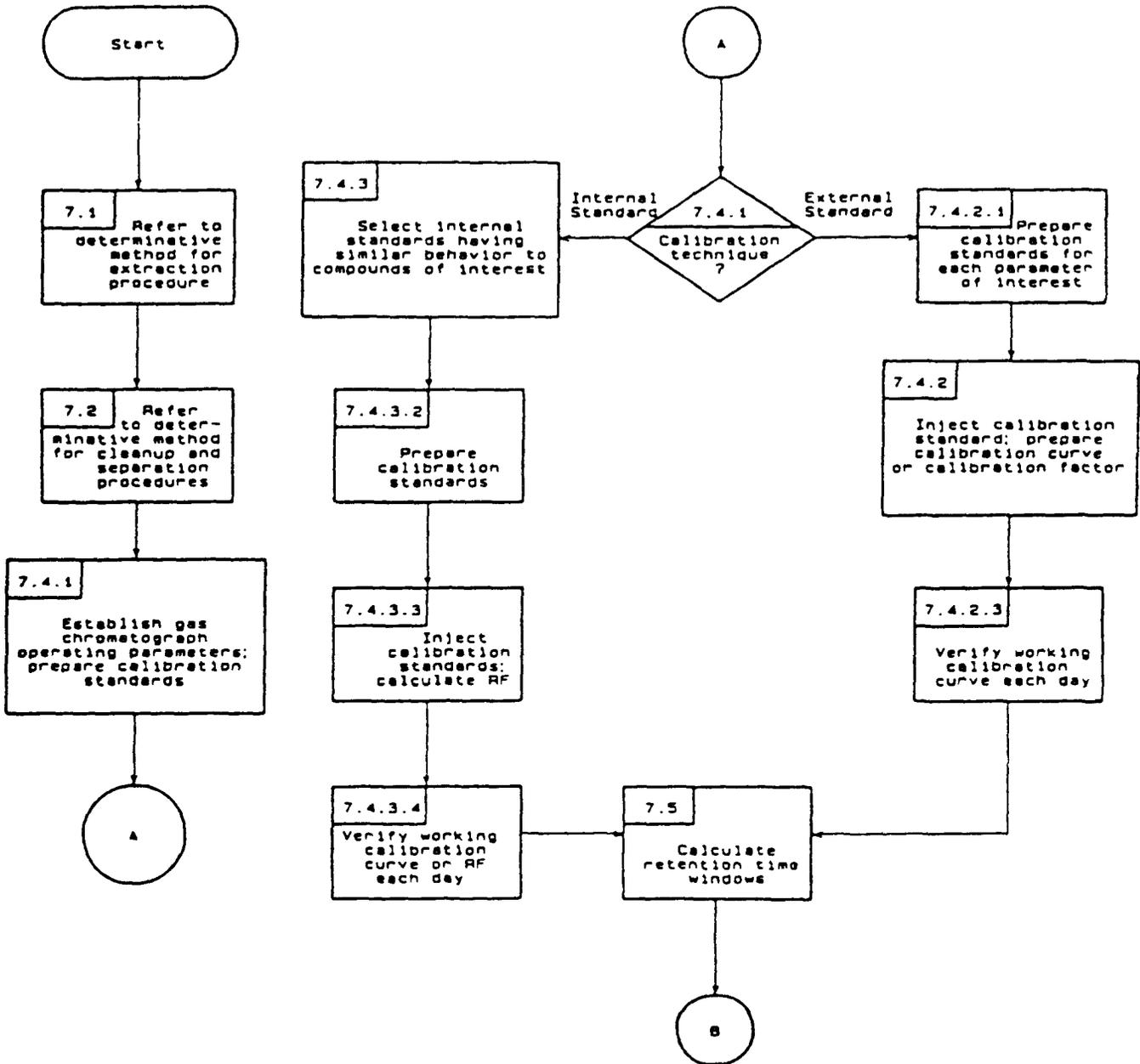
2. U.S. EPA 40 CFR Part 136, Appendix B. "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

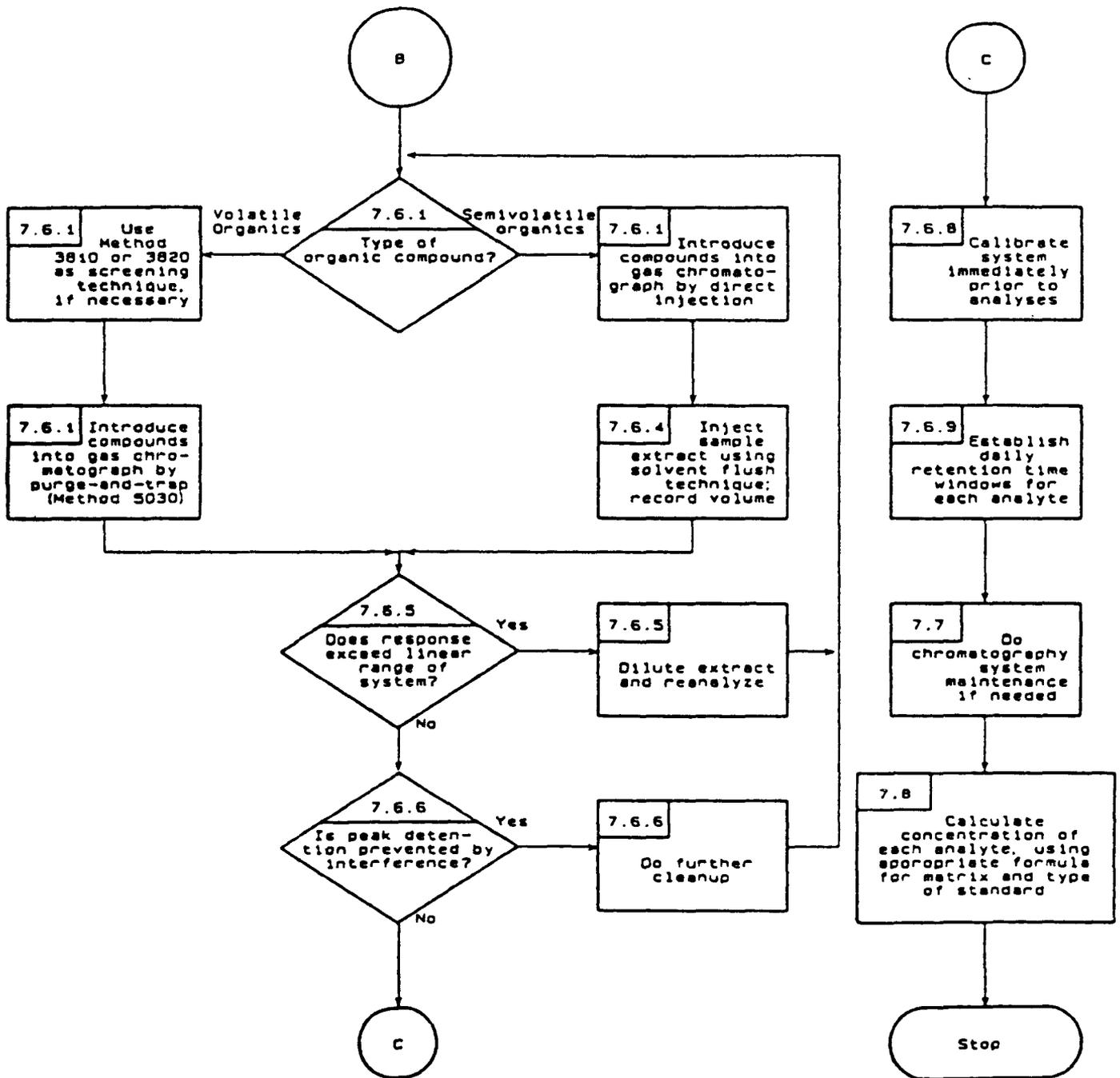
4. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

5. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

METHOD 8000
GAS CHROMATOGRAPHY



METHOD 8000
 GAS CHROMATOGRAPH
 (Continued)



METHOD 8010B

HALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No. ^a	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Allyl chloride	107-05-1	b	b
Benzyl chloride	100-44-7	pp	b
Bis(2-chloroethoxy)methane	111-91-1	pp	pc
Bis(2-chloroisopropyl) ether	39638-32-9	b	b
Bromoacetone	598-31-2	pp	b
Bromobenzene	108-86-1	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
Carbon tetrachloride	56-23-5	b	b
Chloroacetaldehyde	107-20-0	b	b
Chlorobenzene	108-90-7	b	b
Chloroethane	75-00-3	b	b
2-Chloroethanol	107-07-03	pp	b
2-Chloroethyl vinyl ether	110-75-8	b	b
Chloroform	67-66-3	b	b
1-Chlorohexane	544-10-5	pc	pc
Chloromethane	74-87-3	b	b
Chloromethyl methyl ether	107-30-2	pp	pc
Chloroprene	126-99-8	b	b
4-Chlorotoluene	106-43-4	b	b
Dibromochloromethane	124-48-1	b	b
1,2-Dibromo-3-chloropropane	96-12-8	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
1,4-Dichloro-2-butene	764-41-0	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b
Dichloromethane	75-09-2	b	b
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloro-2-propanol	96-23-1	pp	b
cis-1,3-Dichloropropene	10061-01-5	b	b
trans-1,3-Dichloropropene	10061-02-6	b	b

Compound Name	CAS No. ^a	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Epichlorhydrin	106-89-8	pp	b
Ethylene dibromide	106-93-4	b	b
Methyl iodide	74-88-4	pp	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
Tetrachloroethene	127-18-4	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
Vinyl Chloride	75-01-4	b	b

a Chemical Abstract Services Registry Number

b Adequate response using this technique

pp Poor purging efficiency, resulting in high EQLs

pc Poor chromatographic performance.

1.2 Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8010 provides gas chromatographic conditions for the detection of halogenated volatile organic compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a electrolytic conductivity detector (HECD).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from co-eluting non-target compounds and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas chromatograph - analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in. ID stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

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

4.1.3 Detector - Electrolytic conductivity (HECD).

4.2 Sample introduction apparatus, refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes, 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A, Appropriate sizes with ground glass stoppers.

4.5 Microsyringe, 10 and 25 μL with a 0.006 in. ID needle (Hamilton 702N or equivalent) and a 100 μL .

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH . Pesticide quality or equivalent. Store away from other solvents.

5.4 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards 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.

5.4.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.4.2 Add the assayed reference material, as described below.

5.4.2.1 Liquids. Using a 100 μ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.4.2.2 Gases. To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

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

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

5.4.5 Prepare fresh standards every 2 months, for gases or for reactive compounds such as 2-chloroethyl vinyl ether. All other standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.5 Secondary dilution standards. Using stock standard solutions, prepare secondary dilution standards in methanol, as needed, containing the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.6 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.6 Calibration standards. Prepare calibration standards in organic-free reagent water from the secondary dilution of the stock standards, at a minimum of five concentrations. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.6.1 Do not inject more than 20 μL of alcoholic standards into 100 mL of water.

5.6.2 Use a 25 μL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.6.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.6.4 Mix aqueous standards by inverting the flask three times only.

5.6.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.6.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.6.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.7 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. The compounds recommended for use as surrogate spikes (Section 5.8) have been used successfully as internal standards, because of their generally unique retention times.

5.7.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

5.7.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.4 and 5.5. It is recommended that the secondary dilution standard be prepared at a concentration of 15 $\text{ng}/\mu\text{L}$ of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 $\mu\text{g}/\text{L}$.

5.7.3 Analyze each calibration standard according to Section 7.0, adding 10 μL of internal standard spiking solution directly to the syringe.

5.8 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate halocarbons. A combination of bromochloromethane, bromochlorobenzene and bromofluorobenzene is recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.4, add a volume to give 750 μg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 $\text{ng}/\mu\text{L}$. Add 10 μL of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.7.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph using either direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatographic conditions (Recommended)

7.2.1 Column 1:

Helium flow rate = 40 mL/min

Temperature program:

Initial temperature = 45°C, hold for 3 minutes

Program = 45°C to 220°C at 8°C/min

Final temperature = 220°C, hold for 15 minutes.

7.2.2 Column 2:

Helium flow rate = 40 mL/min

Temperature program:

Initial temperature = 50°C, hold for 3 minutes

Program = 50°C to 170°C at 6°C/min

Final temperature = 170°C, hold for 4 minutes.

7.3 Calibration. The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures. Use

Table 1 and Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap) or the direct injection method (see Section 7.4.1.1). If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to purging.

7.4.1.1 In very limited applications (e.g. aqueous process wastes) direct injection of the sample onto the GC column with a 10 μL syringe may be appropriate. The detection limit is very high (approximately 10,000 $\mu\text{g/L}$) therefore, it is only permitted where concentrations in excess of 10,000 $\mu\text{g/L}$ are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two columns for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Refer to Method 8000 for guidance on calculation of concentration.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each analyte of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required:

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or re-analyze the sample if any of the above checks reveal a problem.
- Re-extract and re-analyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0-500 $\mu\text{g/L}$. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte, and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A.; Lichtenberg, J.J. J. Amer. Water Works Assoc. 1974, 66(12), pp. 739-744.
2. Bellar, T.A.; Lichtenberg, J.J., Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, Measurement of Organic Pollutants in Water and Wastewater; Van Hall, Ed.; ASTM STP 686, pp 108-129, 1979.
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. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act: Final Rule and Interim Final Rule and Proposed Rule", October 26, 1984.
5. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)"; Report for EPA Contract 68-03-2856 (in preparation).
5. Gebhart, J.E., S.V. Lucas, S.J. Naber, A.M. Berry, T.H. Danison and H.M. Burkholder, "Validation of SW-846 Methods 8010, 8015, and 8020"; Report for EPA Contract 68-03-1760, Work Assignment 2-15; US EPA, EMSL-Cincinnati, 1987.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR HALOGENATED VOLATILE ORGANICS

Compound	CAS Registry Number	Retention Time (minutes)		Method Detection Limit ^a ($\mu\text{g/L}$)
		Column 1	Column 2	
Ally chloride	107-05-1	10.17	(b)	(b)
Benzyl chloride ^{*,c}	100-44-7	30.29	(b)	(b)
Bis(2-chloroethoxy)methane [*]	111-91-1	38.60	(b)	(b)
Bis(2-chloroisopropyl) ether [*]	39638-32-9	34.79	(b)	(b)
Bromobenzene	108-86-1	29.05	(b)	(b)
Bromodichloromethane	75-27-4	15.44	14.62	0.002
Bromoform	75-25-2	21.12	19.17	0.020
Bromomethane [*]	74-83-9	2.90	7.05	0.030
Carbon tetrachloride [*]	56-23-5	14.58	11.07	0.003
Chloroacetaldehyde [*]	107-20-0	(b)	(b)	(b)
Chlorobenzene	108-90-7	25.49	18.83	0.001
Chloroethane	75-00-3	5.18	8.68	0.008
Chloroform	67-66-3	12.62	12.08	0.002
1-Chlorohexane	544-10-5	26.26	(b)	(b)
2-Chloroethyl vinyl ether [*]	110-75-8	19.23	(b)	0.130
Chloromethane	74-87-3	1.40	5.28	0.010
Chloromethyl methyl ether [*]	107-30-2	8.88	(b)	(b)
4-Chlorotoluene	106-43-4	34.46	(b)	(b)
Dibromochloromethane	124-48-1	18.22	16.62	(b)
1,2-Dibromo-3-chloropropane [*]	96-12-8	28.09	(b)	0.030
Dibromomethane	74-95-3	13.83	14.92	(b)
1,2-Dichlorobenzene [*]	95-50-1	37.96	23.52	(b)
1,3-Dichlorobenzene [*]	541-73-1	36.88	22.43	(b)
1,4-Dichlorobenzene [*]	106-46-7	38.64	22.33	(b)
1,4-Dichloro-2-butene	764-41-0	23.45	(b)	(b)
Dichlorodifluoromethane ^{*,d}	75-71-8	3.68	(b)	(b)
1,1-Dichloroethane [*]	75-34-3	11.21	12.57	0.002
1,2-Dichloroethane [*]	107-06-2	13.14	15.35	0.002
1,1-Dichloroethene [*]	75-35-4	10.04	7.72	0.003
trans-1,2-Dichloroethene [*]	156-60-5	11.97	9.38	0.002
Dichloromethane	75-09-2	7.56	10.12	(b)
1,2-Dichloropropane [*]	78-87-5	16.69	16.62	(b)
trans-1,3-Dichloropropene [*]	10061-02-5	16.97 ^e	16.60	0.340
Ethylene dibromide	106-93-4	19.59	(b)	(b)
1,1,2,2-Tetrachloroethane [*]	79-34-5	23.12	(b)	0.010
1,1,1,2-Tetrachloroethane [*]	630-20-6	21.10	21.70	(b)
Tetrachloroethene	127-18-4	23.05	14.97	0.001
1,1,1-Trichloroethane	71-55-6	14.48	13.10	0.003
1,1,2-Trichloroethane [*]	79-00-5	18.27	18.07	0.007
Trichloroethene	79-01-6	17.40	13.12	0.001
Trichlorofluoromethane [*]	75-69-4	9.26	(b)	(b)
1,2,3-Trichloropropane [*]	96-18-4	22.95	(b)	(b)
Vinyl Chloride	75-01-4	3.25	5.28	0.006

TABLE 1.
Continued

-
- a = Using purge-and-trap method (Method 5030)
 - b = Not determined
 - * = Appendix VIII compounds
 - c = Demonstrated very erratic results when tested by purge-and-trap
 - d = See Section 4.10.2 of Method 5030 for guidance on selection of trapping material
 - e = Estimated retention time

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

^a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

^b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA^a

Analyte	Range for Q ($\mu\text{g/L}$)	Limit for S ($\mu\text{g/L}$)	Range for \bar{x} ($\mu\text{g/L}$)	Range P, P _s (%)
Bromodichloromethane	15.2-24.8	4.3	10.7-32.0	42-172
Bromoform	14.7-25.3	4.7	5.0-29.3	13-159
Bromomethane	11.7-28.3	7.6	3.4-24.5	D-144
Carbon tetrachloride	13.7-26.3	5.6	11.8-25.3	43-143
Chlorobenzene	14.4-25.6	5.0	10.2-27.4	38-150
Chloroethane	15.4-24.6	4.4	11.3-25.2	46-137
2-Chloroethylvinyl ether	12.0-28.0	8.3	4.5-35.5	14-186
Chloroform	15.0-25.0	4.5	12.4-24.0	49-133
Chloromethane	11.9-28.1	7.4	D-34.9	D-193
Dibromochloromethane	13.1-26.9	6.3	7.9-35.1	24-191
1,2-Dichlorobenzene	14.0-26.0	5.5	1.7-38.9	D-208
1,3-Dichlorobenzene	9.9-30.1	9.1	6.2-32.6	7-187
1,4-Dichlorobenzene	13.9-26.1	5.5	11.5-25.5	42-143
1,1-Dichloroethane	16.8-23.2	3.2	11.2-24.6	47-132
1,2-Dichloroethane	14.3-25.7	5.2	13.0-26.5	51-147
1,1-Dichloroethene	12.6-27.4	6.6	10.2-27.3	28-167
trans-1,2-Dichloroethene	12.8-27.2	6.4	11.4-27.1	38-155
Dichloromethane	15.5-24.5	4.0	7.0-27.6	25-162
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	41-138
1,1,2-Trichloroethane	15.7-24.3	3.9	9.6-25.4	39-136
Trichloroethene	15.4-24.6	4.2	9.2-26.6	35-146
Trichlorofluoromethane	13.3-26.7	6.0	7.4-28.1	21-156
Vinyl chloride	13.7-26.3	5.7	8.2-29.9	28-163

Q = Concentration measured in QC check sample, in $\mu\text{g/L}$.

s = Standard deviation of four recovery measurements, in $\mu\text{g/L}$.

X = Average recovery for four recovery measurements, in $\mu\text{g/L}$.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

^a Criteria from 40 CFR Part 136 for Method 601 and were calculated assuming a QC check sample concentration of 20 $\mu\text{g/L}$.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION^a

Analyte	Accuracy, as recovery, x' ($\mu\text{g/L}$)	Single analyst precision, s_r' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Bromodichloromethane	1.12C-1.02	0.11X+0.04	0.20X+1.00
Bromoform	0.96C-2.05	0.12X+0.58	0.21X+2.41
Bromomethane	0.76C-1.27	0.28X+0.27	0.36X+0.94
Carbon tetrachloride	0.98C-1.04	0.15X+0.38	0.20X+0.39
Chlorobenzene	1.00C-1.23	0.15X-0.02	0.18X+1.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X+0.63
2-Chloroethyl vinyl ether ^b	1.00C	0.20X	0.35X
Chloroform	0.93C-0.39	0.13X+0.15	0.19X-0.02
Chloromethane	0.77C+0.18	0.28X-0.31	0.52X+1.31
Dibromochloromethane	0.94C+2.72	0.11X+1.10	0.24X+1.68
1,2-Dichlorobenzene	0.93C+1.70	0.20X+0.97	0.13X+6.13
1,3-Dichlorobenzene	0.95C+0.43	0.14X+2.33	0.26X+2.34
1,4-Dichlorobenzene	0.93C-0.09	0.15X+0.29	0.20X+0.41
1,1-Dichloroethane	0.95C-1.08	0.08X+0.17	0.14X+0.94
1,2-Dichloroethane	1.04C-1.06	0.11X+0.70	0.15X+0.94
1,1-Dichloroethene	0.98C-0.87	0.21X-0.23	0.29X-0.04
trans-1,2-Dichloroethene	0.97C-0.16	0.11X+1.46	0.17X+1.46
Dichloromethane	0.91C-0.93	0.11X+0.33	0.21X+1.43
1,2-Dichloropropane ^b	1.00C	0.13X	0.23X
cis-1,3-Dichloropropene ^b	1.00C	0.18X	0.32X
trans-1,3-Dichloropropene ^b	1.00C	0.18X	0.32X
1,1,2,2-Tetrachloroethane	0.95C+0.19	0.14X+2.41	0.23X+2.79
Tetrachloroethene	0.94C+0.06	0.14X+0.38	0.18X+2.21
1,1,1-Trichloroethane	0.90C-0.16	0.15X+0.04	0.20X+0.37
1,1,2-Trichloroethane	0.86C+0.30	0.13X-0.14	0.19X+0.67
Trichloroethene	0.87C+0.48	0.13X-0.03	0.23X+0.30
Trichlorofluoromethane	0.89C-0.07	0.15X+0.67	0.26X+0.91
Vinyl chloride	0.97C-0.36	0.13X+0.65	0.27X+0.40

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in $\mu\text{g/L}$.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of x, in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of x, in $\mu\text{g/L}$.

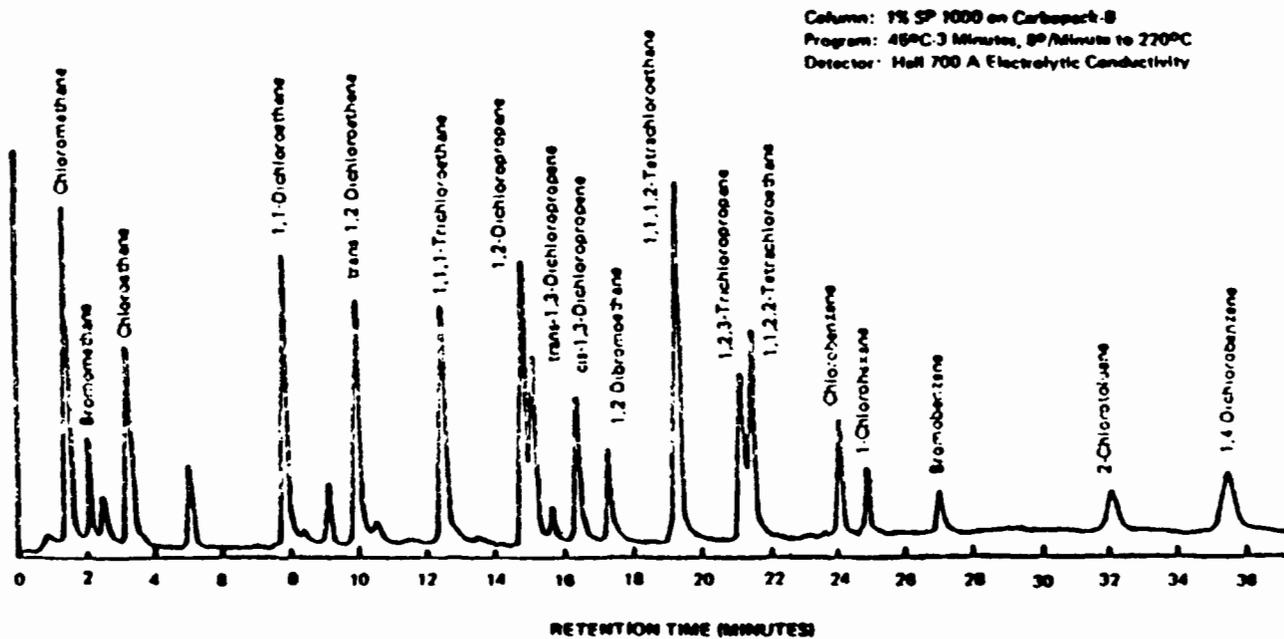
C = True value for the concentration, in $\mu\text{g/L}$.

X = Average recovery found for measurements of samples containing a concentration of C, in $\mu\text{g/L}$.

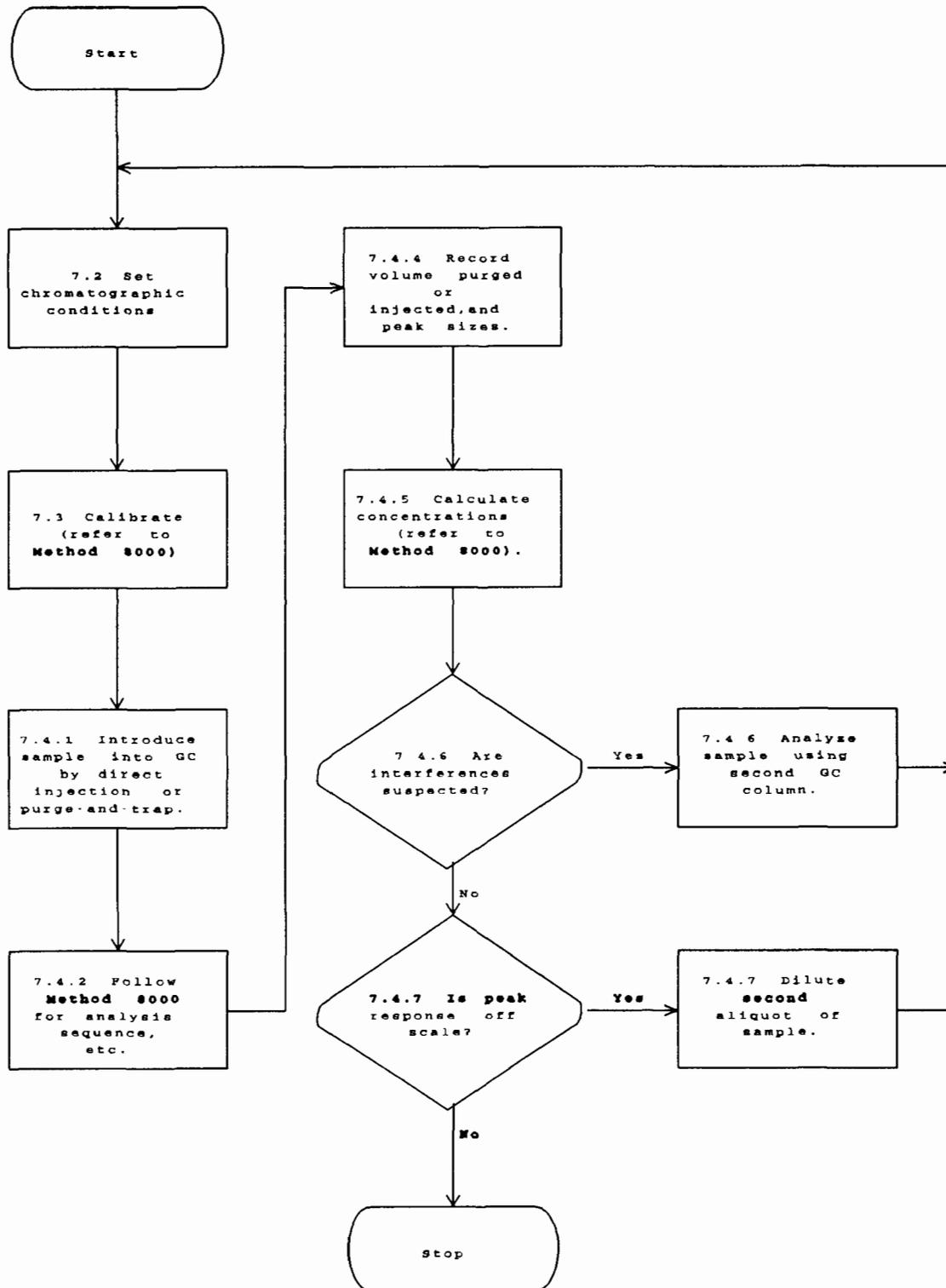
^a From 40 CFR Part 136 for Method 601.

^b Estimates based upon the performance in a single laboratory.

FIGURE 1.
GAS CHROMATOGRAM OF HALOGENATED VOLATILE ORGANICS



METHOD 8010B
HALOGENATED VOLATILE ORGANICS BY GAS CHROMATOGRAPHY



Method 8011

1,2-DIBROMOETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE IN WATER BY MICROEXTRACTION AND GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of the following compounds in drinking water and ground water:

<u>Analyte</u>	<u>Chemical Abstracts Service Registry Number</u>
1,2-Dibromoethane (EDB)	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8

1.2 For compounds other than the above mentioned analytes, or for other matrices, the laboratory must demonstrate the usefulness of the method by collecting precision and accuracy data on actual samples and provide qualitative confirmation of results by gas chromatography/mass spectrometry (GC/MS).

1.3 The experimentally determined method detection limits (MDL) for EDB and DBCP were calculated to be 0.01 ug/L. The method has been shown to be useful for these analytes over a concentration range from approximately 0.03 to 200 ug/L. Actual detection limits are highly dependent upon the characteristics of the gas chromatographic system, sample matrix, and calibration.

1.4 This method is restricted to use by or under the Supervision of analysts experienced in the use of gas chromatography and in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Step 8.2.

1.5 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

2.0 SUMMARY OF METHOD

2.1 Thirty five mL of sample are extracted with 2 mL of hexane. Two uL of the extract are then injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis. Aqueous matrix spikes are extracted and analyzed in an identical manner as the samples in order to compensate for possible extraction losses.

2.2 The extraction and analysis time is 30 to 50 minutes per sample depending upon the analytical conditions chosen. See Table 1 and Figure 1.

2.3 Confirmatory evidence is obtained using a different column (Table 1).

3.0 INTERFERENCES

3.1 Impurities contained in the extracting solvent (hexane) usually account for the majority of the analytical problems. Reagent blanks should be analyzed on each new bottle of hexane before use. Indirect daily checks on the hexane are obtained by monitoring the calibration and reagent blanks. Whenever an interference is noted in the method or instrument blank, the laboratory should reanalyze the hexane. Low level interferences generally can be removed by distillation or column chromatography however, it is generally more economical to obtain a new source of hexane solvent. Interference-free hexane is defined as containing less than 0.01 ug/L of the analytes. Protect interference-free hexane by storing it in an area known to be free of organochlorine solvents.

3.2 Several instances of accidental sample contamination have been attributed to diffusion of volatile organics through the septum seal into the sample bottle during shipment and storage. Field blanks must be used to monitor for this problem.

3.3 This liquid/liquid extraction technique extracts a wide boiling range of non-polar organic compounds and, in addition, extracts some polar organic compounds.

3.4 EDB at low concentrations may be masked by very high levels of dibromochloromethane (DBCM), a common chlorinated drinking water contaminant, when using the confirmation column.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringe - 10, 25, and 100 uL with a 2 in x 0.006 in needle (Hamilton 702N or equivalent).

4.2 Gas Chromatograph

4.2.1 The GC must be capable of temperature programming and should be equipped with a linearized electron capture detector and a capillary column splitless injector.

4.2.2 Two gas chromatography columns are recommended. Column A is a highly efficient column that provides separations for EDB and DBCP without interferences from trihalomethanes. Column A should be used as the primary analytical column unless routinely occurring analytes are not adequately resolved. Column B is recommended for use as a confirmatory column when GC/MS confirmation is not available. Retention times for EDB and DBCP on these columns are presented in Table 1.

4.2.3 Column A - 0.32 mm i.d. x 30 m fused silica capillary with dimethyl silicone mixed phase (Durawax-DX 3, 0.25 um film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 minutes, then increase to 190°C at 8°C/min, and hold at 190°C for 25 minutes or until

all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. See Figure 1 for a sample chromatogram and Table 1 for retention data.

4.2.4 Column B (confirmation column) - 0.32 mm i.d. x 30 m fused silica capillary with methyl polysiloxane phase (DB-1, 0.25 µm film, or equivalent). The linear velocity of the helium carrier gas is established at 25 cm/sec. The column temperature is programmed to hold at 40°C for 4 minutes, then increase to 270°C at 10°C/min, and hold at 270°C for 10 minutes or until all expected compounds have eluted. Injector temperature: 200°C. Detector temperature: 290°C. See Table 1 for retention data.

5.0 REAGENTS

5.1 Hexane, C₆H₁₄. UV grade (Burdick and Jackson #216 or equivalent).

5.2 Methyl alcohol, CH₃OH. Demonstrated to be free of analytes.

5.3 Sodium chloride, NaCl. Pulverize a batch of NaCl and place it in a muffle furnace at room temperature. Increase the temperature to 400°C for 30 minutes. Place it in a bottle and cap.

5.4 1,2-Dibromoethane (99%), C₂H₄Br₂, (Aldrich Chemical Company).

5.5 1,2-Dibromo-3-chloropropane (99.4%), C₃H₅Br₂Cl, (AMVAC Chemical Corporation, Los Angeles, California).

5.6 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. Must be free of interferences at the method detection limit (MDL) of the analytes of interest. ASTM Type II water is further purified by any of the following techniques:

5.6.1 Water may be generated by passing tap water through a carbon filter bed containing about 453 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.6.2 A water purification system (Millipore Milli-Q Plus with the Organex-Q cartridge or equivalent) may be used to generate water.

5.6.3 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 1 hour. While it is still hot, transfer the water to a narrow-mouth screw-cap bottle and seal with a Teflon lined septum and cap.

5.7 Stock standards - These solutions may be purchased as certified solutions or prepared from pure standards using the following procedures:

5.7.1 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 and weigh to the nearest 0.1 mg.

5.7.2 Use a 25- μ L syringe and immediately add two or more drops (≈ 10 μ L) of standard to the flask. Be sure that the standard falls directly into the alcohol without contacting the neck of the flask.

5.7.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter from the net gain in weight (approximately 1000 μ g/L).

5.7.4 Store stock standards in 15-mL bottles equipped with PTFE lined screw-caps. Stock standards are stable for at least four weeks when stored at 4°C and away from light.

5.8 Intermediate standard - Use stock standards to prepare an intermediate standard that contains both analytes in methanol. The intermediate standard should be prepared at a concentration that can be easily diluted to prepare aqueous calibration standards that will bracket the working concentration range. Store the intermediate standard with minimal headspace and check frequently for signs of deterioration or evaporation, especially just before preparing calibration standards. The storage time described for stock standards also applies to the intermediate standard.

5.9 Quality control (QC) reference sample - Prepare a QC reference sample concentrate at 0.25 μ g/mL of both analytes from standards from a different source than the standards used for the stock standard.

5.10 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.11 Check standard - Add an appropriate volume of the intermediate standard to an aliquot of water in a volumetric flask. Do not add less than 20 μ L of an alcoholic intermediate standard to the water or poor precision will result. Use a 25- μ L microsyringe and rapidly inject the alcoholic intermediate standard into the expanded area of the almost filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask several times. Discard the contents contained in the neck of the flask. Aqueous calibration standards should be prepared every 8 hours.

6.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Calibration

7.1.1 At least five calibration standards are needed. One should contain EDB and DBCP at a concentration near, but greater than, the method

detection limit (Table 1) for each compound. The others should be at concentrations that bracket the range expected in samples. For example, if the MDL is 0.01 ug/L, and a sample expected to contain approximately 0.10 ug/L is to be analyzed, aqueous calibration standards should be prepared at concentrations of 0.03 ug/L, 0.05 ug/L, 0.10 ug/L, 0.15 ug/L, and 0.20 ug/L.

7.1.2 Analyze each calibration standard and tabulate peak height or area response versus the concentration in the standard. Prepare a calibration curve for each compound. Alternatively, if the ratio of response to concentration (calibration factor) is a constant over the working range (< 10% relative standard deviation), linearity can be assumed and the average ratio or calibration factor can be used in place of a calibration curve.

7.2 Sample preparation

7.2.1 Remove samples and standards from storage and allow them to reach room temperature.

7.2.2 For samples and field blanks contained in 40-mL bottles, remove the container cap. Discard a 5-mL volume using a 5-mL transfer pipet. Replace the container cap and weigh the container with contents to the nearest 0.1 g and record this weight for subsequent sample volume determination.

7.2.3 For calibration standards, check standards, QC reference samples, and blanks, measure a 35-mL volume using a 50-mL graduated cylinder and transfer it to a 40-mL sample container.

7.3 Extraction

7.3.1 Remove the container cap and add 7 g of NaCl to all samples.

7.3.2 Recap the sample container and dissolve the NaCl by shaking by hand for about 20 seconds.

7.3.3 Remove the cap and using a transfer pipet, add 2.0 mL of hexane. Recap and shake vigorously by hand for 1 minute. Allow the water and hexane phases to separate. If stored at this stage, keep the container upside down.

7.3.4 Remove the cap and carefully transfer a sufficient amount (0.5-1.0 mL) of the hexane layer into a vial using a disposable glass pipet.

7.3.5 Transfer the remaining hexane phase, being careful not to include any of the water phase, into a second vial. Reserve this second vial at 4°C for reanalysis if necessary.

7.4 Analysis

7.4.1 Transfer the first sample vial to an autosampler set up to inject 2.0 uL portions into the gas chromatograph for analysis. Alternately, 2 uL portions of samples, blanks and standards may be manually injected, although an auto sampler is strongly recommended.

7.5 Determination of sample volume

7.5.1 For samples and field blanks, remove the cap from the sample container. Discard the remaining sample/hexane mixture. Shake off the remaining few drops using short, brisk wrist movements. Reweigh the empty container with original cap and calculate the net weight of sample by difference to the nearest 0.1 g. This net weight is equivalent to the volume of water extracted.

7.6 Calculations

7.6.1 Identify EDB and DBCP in the sample chromatogram by comparing the retention time of the suspect peak to retention times generated by the calibration standards and the check standard.

7.6.2 Use the calibration curve or calibration factor to directly calculate the uncorrected concentration (C_i) of each analyte in the sample (e.g. calibration factor x response).

7.6.3 Calculate the sample volume (V_S) as equal to the net sample weight:

$$V_S \text{ (mL)} = \text{gross weight (grams)} - \text{bottle tare (grams)}$$

7.6.4 Calculate the corrected sample concentration as:

$$\text{Concentration (ug/L)} = C_i \times \frac{35}{V_S}$$

7.6.5 Report the results for the unknown samples in ug/L. Round the results to the nearest 0.01 ug/L or two significant figures.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program.

8.1.1 The laboratory must make an initial determination of the method detection limits and demonstrate the ability to generate acceptable accuracy and precision with this method. This is established as described in Step 8.2.

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

modification is made to the method, the analyst is required to repeat the procedure in Steps 7.1 and 8.2.

8.1.3 The laboratory must analyze a reagent and calibration blank to demonstrate that interferences from the analytical system are under control every twenty samples or per analytical batch whichever is more frequent.

8.1.4 The laboratory must, on an ongoing basis, demonstrate through the analyses of QC reference samples and check standards that the operation of the measurement system is in control. The frequency of the check standard analyses is equivalent to 5% of all samples or every analytical batch, whichever is more frequent. On a weekly basis, the QC reference sample must be run.

8.2 To establish the ability to achieve low detection limits and generate acceptable accuracy and precision, the analyst must perform the following operations:

8.2.1 Prepare seven samples each at a concentration of 0.03 ug/L.

8.2.2 Analyze the samples according to the method beginning in Section 7.0.

8.2.3 Calculate the average concentration (\bar{X}) in ug/L and the standard deviation of the concentrations (s) in ug/L, for each analyte using the seven results. Then calculate the MDL at 99% confidence level for seven replicates as $3.143s$.

8.2.4 For each analyte in an aqueous matrix sampler, \bar{X} must be between 60% and 140% of the true value. Additionally, the MDL may not exceed the 0.03 ug/L spiked concentration. If both analytes meet the acceptance criteria, the system performance is acceptable and analysis of actual samples can begin. If either analyte fails to meet a criterion, repeat the test. It is recommended that the laboratory repeat the MDL determination on a regular basis.

8.3 The laboratory must demonstrate on a frequency equivalent to 5% of the sample load or once per analytical batch, whichever is more frequent, that the measurement system is in control by analyzing a check standard of both analytes at 0.25 ug/L.

8.3.1 Prepare a check standard (0.25 ug/L) by diluting the intermediate standard with water to 0.25 ug/L.

8.3.2 Analyze the sample according to Section 7.0 and calculate the recovery for each analyte. The recovery must be between 60% and 140% of the expected value for aqueous matrices. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.3.3 If the recovery for either analyte falls outside the designated range, the analyte fails the acceptance criteria. A second calibration verification standard containing each analyte that failed must

be analyzed. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test.

8.4 On a weekly basis, the laboratory must demonstrate the ability to analyze a QC reference sample.

8.4.1 Prepare a QC reference sample at 0.10 ug/L by diluting the QC reference sample concentrate (Step 5.9).

8.4.2 For each analyte in an aqueous matrix, the recovery must be between 60% and 140% of the expected value. When either analyte fails the test, the analyst must repeat the test only for that analyte which failed to meet the criteria. Repeated failure, however, will confirm a general problem with the measurement system or faulty samples and/or standards. If this occurs, locate and correct the source of the problem and repeat the test. For non-aqueous matrices, the U.S. EPA will set criteria after more interlaboratory data are gathered.

8.5 Instrument performance - Check the performance of the entire analytical system daily using data gathered from analyses of blanks, standards, and replicate samples.

8.5.1 Peak tailing significantly in excess of that shown in the chromatogram (Figure 1) must be corrected. Tailing problems are generally traceable to active sites on the GC column or to the detector operation.

8.5.2 Check the precision between replicate analyses. A properly operating system should perform with an average relative standard deviation of less than 10%. Poor precision is generally traceable to pneumatic leaks, especially at the injection port.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision at several concentrations in tap water are presented in Table 2. The method detection limits are presented in Table 1.

9.2 In a preservation study extending over a 4 week period, the average percent recoveries and relative standard deviations presented in Table 3 were observed for reagent water (acidified), tap water and ground water. The results for acidified and non-acidified samples were not significantly different.

10.0 REFERENCES

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TABLE 1.
 CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION
 LIMITS (MDL) FOR 1,2-DIBROMOETHANE (EDB) AND
 1,2-DIBROMO-3-CHLOROPROPANE (DBCP)

Analyte	Retention Time, Minutes		MDL (ug/L)
	Column A	Column B	
EDB	9.5	8.9	0.01
DBCP	17.3	15.0	0.01

Column A: Durawax-DX 3
 Column B: DB-1

TABLE 2.
 SINGLE LABORATORY ACCURACY AND PRECISION
 FOR EDB AND DBCP IN TAP WATER

Analyte	Number of Samples	Spike Level (ug/L)	Average Recovery (%)	Relative Standard Deviation (%)
EDB	7	0.03	114	9.5
	7	0.24	98	11.8
	7	50.0	95	4.7
DBCP	7	0.03	90	11.4
	7	0.24	102	8.3
	7	50.0	94	4.8

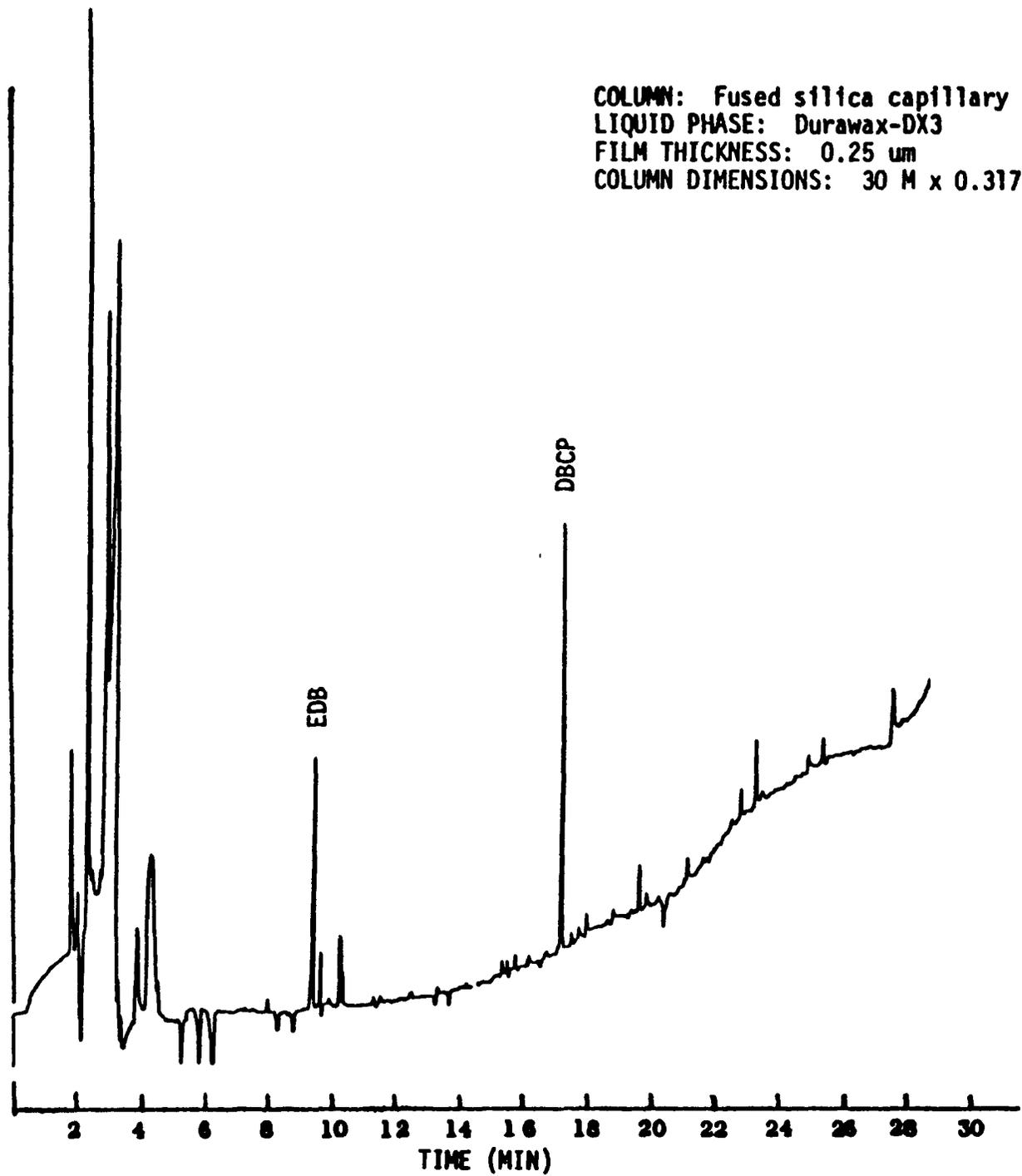
TABLE 3.
ACCURACY AND PRECISION AT 2.0 ug/L
OVER A 4-WEEK STUDY PERIOD

Analyte	Matrix ¹	Number of Samples	Average Accuracy (% Recovery)	Relative Std. Dev. (%)
EDB	RW-A	16	104	4.7
	GW	15	101	2.5
	GW-A	16	96	4.7
	TW	16	93	6.3
	TW-A	16	93	6.1
DBCP	RW-A	16	105	8.2
	GW	16	105	6.2
	GW-A	16	101	8.4
	TW	16	95	10.1
	TW-A	16	94	6.9

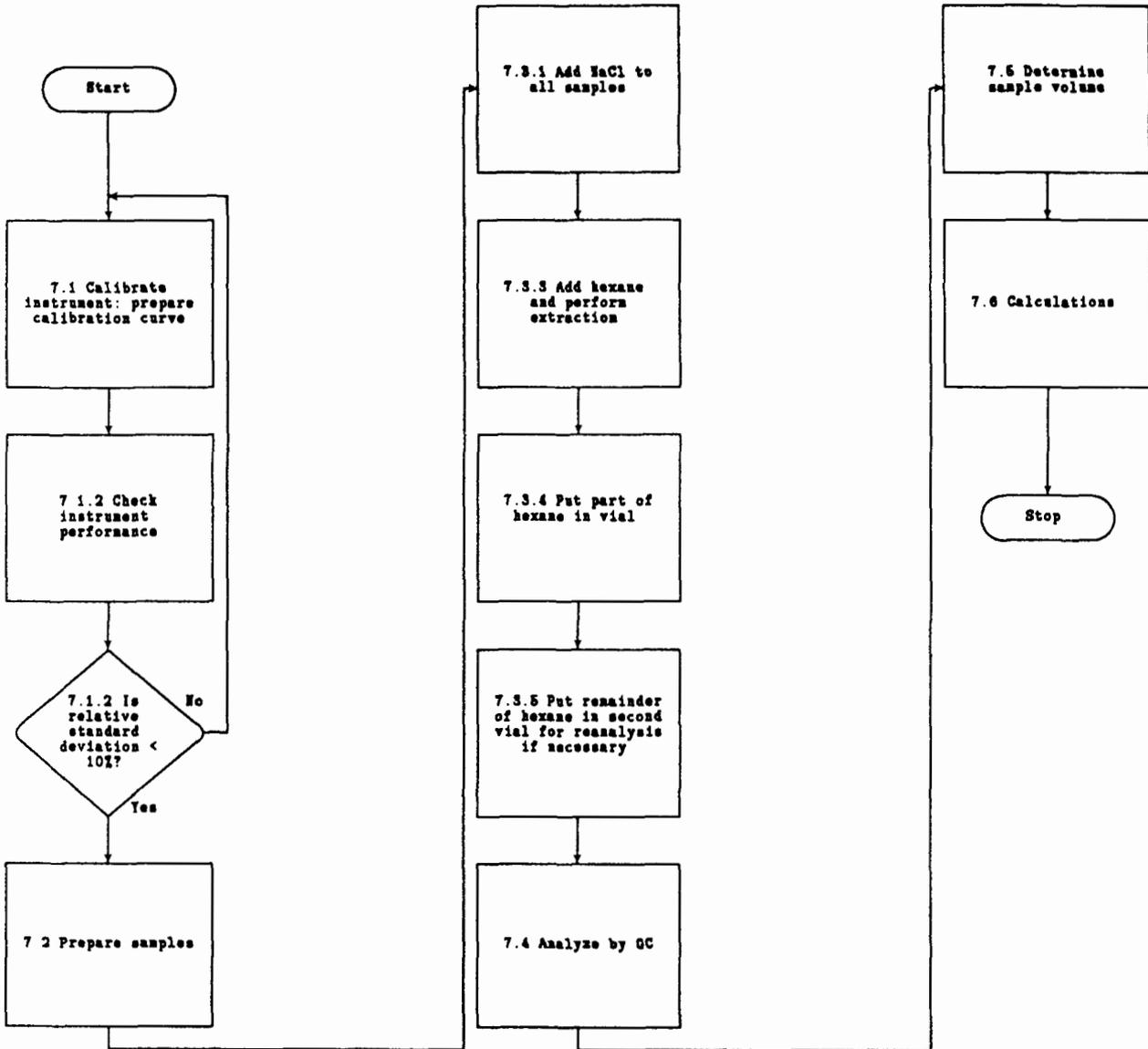
¹Matrix Identities

- RW-A = Reagent water at pH 2
- GW = Ground water, ambient pH
- GW-A = Ground water at pH 2
- TW = Tap water, ambient pH
- TW-A = Tap water at pH 2

FIGURE 1.
SAMPLE CHROMATOGRAM FOR EXTRACT OF WATER SPIKED
AT 0.114 ug/L WITH EDB AND DBCP



METHOD 8011
1,2-DIBROMOMETHANE AND 1,2-DIBROMO-3-CHLOROPROPANE IN WATER
BY MICROEXTRACTION AND GAS CHROMATOGRAPHY



METHOD 8015

NONHALOGENATED VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8015 is used to determine the concentration of various nonhalogenated volatile organic compounds. Table 1 indicates the compounds that may be investigated by this method.

2.0 SUMMARY OF METHOD

2.1 Method 8015 provides gas chromatographic conditions for the detection of certain nonhalogenated volatile organic compounds. Samples may be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed by Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 8 ft x 0.1 in i.d. stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in i.d. stainless steel or glass column packed with n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 Detector - Flame ionization (FID).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flasks - 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringes - 10- and 25- μ L with a 0.006-in i.d. needle (Hamilton 702N or equivalent) and a 100- μ L.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids.

5.3.1 Place about 9.8 mL of methanol in a 10-mL tared 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.

5.3.2 Using a 100- μ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

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

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

5.3.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards - Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Step 5.5 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards - Calibration standards at a minimum of five concentration levels are prepared in water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g. some or all of the compounds listed in Table 1 may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

5.5.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of water.

5.5.2 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hour, unless properly sealed and stored. The aqueous standards can be stored up to 24 hours, if held in sealed vials with zero headspace.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Step 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Steps 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and water blank with one or two surrogate compounds recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Step 5.3, add a volume to give 750 ug of each surrogate to 45 mL of water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Step 5.6.2).

5.7 Methanol, CH₃OH. Pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this Chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For medium-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Column 1 - Set helium gas flow at 40 mL/min flow rate. Set column temperature at 45°C for 3 minutes; then program an 8°C/min temperature rise to 220°C and hold for 15 minutes.

7.2.2 Column 2 - Set helium gas flow at 40 mL/min flow rate. 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.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Step 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC system with a 10-uL syringe may be appropriate. One such application is for verification of the alcohol content of an aqueous sample prior to determining if the sample is ignitable (Methods 1010 or 1020). In this case, it is suggested that direct injection be used. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted when concentrations in excess of 10,000 ug/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.4 Calculation of concentration is covered in Step 7.8 of Method 8000.

7.4.5 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.6 If the response for a peak is off-scale, prepare a dilution of the sample with water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Mandatory quality control to validate the GC system operation is found in Method 8000, Step 8.6.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following is required:

- Check to be sure there are no errors in calculations, surrogate solutions, and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and calibration procedures used.

9.2 Specific method performance information will be provided as it becomes available.

10.0 REFERENCES

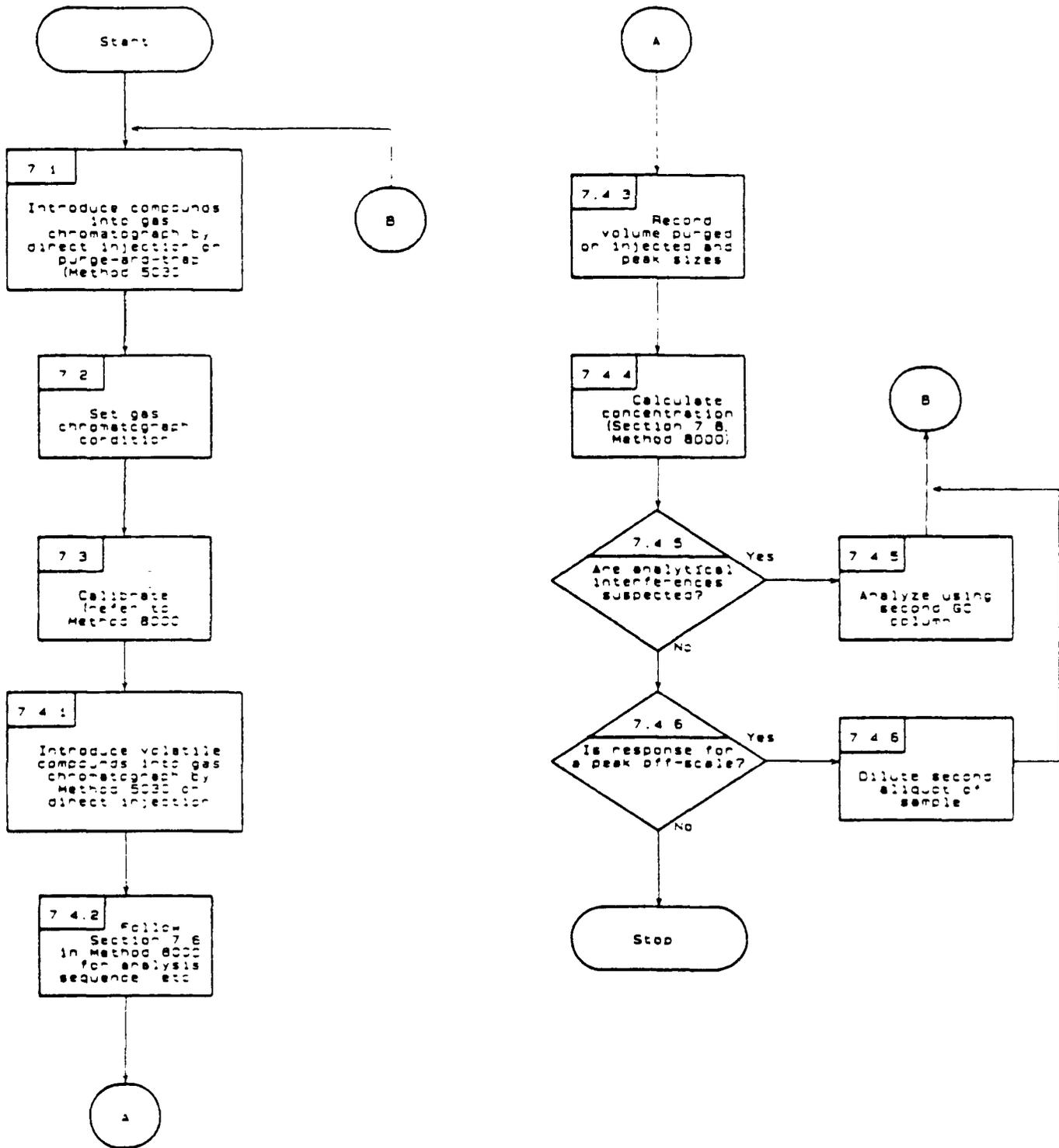
1. Bellar, T.A., and J.J. Lichtenberg, Determining Volatile Organics at Microgram-per-Liter Levels by Gas Chromatography, J. Amer. Water Works Assoc., 66(12), pp. 739-744 (1974).
2. Bellar, T.A., and J.J. Lichtenberg, Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds, in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.
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. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
5. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
NONHALOGENATED VOLATILE ORGANICS

Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)

METHOD 8015
 NONHALOGENATED VOLATILE ORGANICS



METHOD 8020A

AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. The following compounds can be determined by this method:

Compound Name	CAS No. ^a	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Chlorobenzene	108-90-7	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Ethylbenzene	100-41-4	b	b
Toluene	108-88-3	b	b
Xylenes		b	b

a Chemical Abstract Services Registry Number.

b adequate response by this technique.

1.2 Table 1 lists the method detection limit for each target analyte in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8020 provides chromatographic conditions for the detection of aromatic volatile compounds. Samples can be introduced into the GC using direct injection or purge-and-trap (Method 5030). Ground water samples must be determined using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photo-ionization detector (PID).

2.2 If interferences are encountered, the method provides an optional gas chromatographic column that may be helpful in resolving the analytes from the interferences and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Method 5030 and 8000.

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: 6 ft x 0.082 in ID #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcoport, or equivalent.

4.1.2.2 Column 2: 8 ft x 0.1 in ID stainless steel or glass column packed with 5% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 mesh Chromosorb W-AW, or equivalent.

4.1.3 Detector - Photoionization (PID) (h-Nu Systems, Inc. Model PI-51-02 or equivalent).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5 mL Luerlok glass hypodermic and a 5 mL, gas-tight with shutoff valve.

4.4 Volumetric flask, Class A - Appropriate sizes with ground glass stoppers.

4.5 Microsyringe - 10 and 25 μ L with a 0.006 in ID needle (Hamilton 702N or equivalent) and a 100 μ L.

4.6 Analytical balance - 0.0001 g.

5.0 REAGENTS

5.1 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol (CH_3OH) - pesticide quality or equivalent. Store away from other solvents.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids. Because of the toxicity of benzene and 1,4-dichlorobenzene, primary dilutions of these materials should be prepared in a hood.

5.3.1 Place about 9.8 mL of methanol in a 10 mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.3.2 Using a 10 μ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

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

5.3.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.3.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards: Using stock standard solutions, prepare in methanol secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method (e.g., some or all of the compounds listed in the target analyte list may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Do not inject more than 20 μ L of alcoholic standards into 100 mL of organic-free reagent water.

5.5.2 Use a 25 μL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.5.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.5.4 Mix aqueous standards by inverting the flask three times only.

5.5.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.5.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.7 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples. Alpha,alpha,alpha-trifluorotoluene has been used successfully as an internal standard.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each parameter of interest as described in Section 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 mg/L of each internal standard compound. The addition of 10 μL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 $\mu\text{g/L}$.

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10 μL of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with surrogate compounds (bromochlorobenzene, bromofluorobenzene, 1,1,1-trifluorotoluene, fluorobenzene, and difluorobenzene are recommended) which encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.3, add a volume to give 750 μg of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/ μL . Add 10 μL of this surrogate spiking solution directly into the 5 mL syringe with

every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.6.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis. Method 5030 also provides guidance on the analysis of aqueous miscible and non-aqueous miscible liquid wastes (see Section 7.4.1.1 below).

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (He) flow rate: 36 mL/min
For lower boiling compounds:
Initial temperature: 50°C, hold for 2 min;
Temperature program: 50°C to 90°C at 6°C/min, hold until all compounds have eluted.
For higher boiling range of compounds:
Initial temperature: 50°C, hold for 2 min;
Temperature program: 50°C to 110°C at 3°C/min, hold until all compounds have eluted.

Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 Column 2:

Carrier gas (He) flow rate: 30 mL/min
Initial temperature: 40°C, hold for 2 min;
Temperature program: 40°C to 100°C at 2°C/min, hold until all compounds have eluted.

Column 2, an extremely high polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, because resolution between some of the aromatics is not as efficient as with Column 1, Column 2 should be used as a confirmatory column.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis:

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 μL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC system with a 10 μL syringe may be appropriate. The detection limit is very high (approximately 10,000 $\mu\text{g/L}$); therefore, it is only permitted when concentrations in excess of 10,000 $\mu\text{g/L}$ are expected or for water soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

Non-aqueous miscible wastes may also be analyzed by direct injection if the concentration of target analytes in the sample falls within the calibration range. If dilution of the sample is necessary, follow the guidance for High Concentration samples in Method 5030A, Section 7.3.3.2.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. An example of the separation achieved by Column 1 is shown in Figure 1. Figure 2 shows an example of the separation achieved using Column 2.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be

performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each parameter of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure that there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 This method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1 - 500 $\mu\text{g/L}$. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.
2. Bellar, T.A., and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds", in Van Hall (ed.), Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.
3. Dowty, B.J., S.R. Antoine, and J.L. Laseter, "Quantitative and Qualitative Analysis of Purgeable Organics by High Resolution Gas Chromatography and Flame Ionization Detection", in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater. ASTM STP 686, pp. 24-35, 1979.
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).
5. "EPA Method Validation Study 24, Method 602 (Purgeable Aromatics)", Report for EPA Contract 68-03-2856 (in preparation).
6. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule", October 26, 1984.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS
FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min)		Method detection limit ^a (µg/L)
	Col. 1	Col. 2	
Benzene	3.33	2.75	0.2
Chlorobenzene ^b	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

a Using purge-and-trap method (Method 5030).

b Chlorobenzene and m-xylene may co-elute on some columns.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs)
FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

b $EQL = [\text{Method detection limit (Table 1)}] \times [\text{Factor (Table 2)}]$. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
QC ACCEPTANCE CRITERIA^a

Parameter	Range for Q ($\mu\text{g/L}$)	Limit for s ($\mu\text{g/L}$)	Range for \bar{x} ($\mu\text{g/L}$)	Range P, P _s (%)
Benzene	15.4-24.6	4.1	10.0-27.9	39-150
Chlorobenzene	16.1-23.9	3.5	12.7-25.4	55-135
1,2-Dichlorobenzene	13.6-26.4	5.8	10.6-27.6	37-154
1,3-Dichlorobenzene	14.5-25.5	5.0	12.8-25.5	50-141
1,4-Dichlorobenzene	13.9-26.1	5.5	11.6-25.5	42-143
Ethylbenzene	12.6-27.4	6.7	10.0-28.2	32-160
Toluene	15.5-24.5	4.0	11.2-27.7	46-148

Q = Concentration measured in QC check sample, in $\mu\text{g/L}$.

s = Standard deviation of four recovery measurements, in $\mu\text{g/L}$.

\bar{x} = Average recovery for four recovery measurements, in $\mu\text{g/L}$.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

a Criteria from 40 CFR Part 136 for Method 602, and were calculated assuming as check sample concentration of 20 $\mu\text{g/L}$. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 1.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' ($\mu\text{g/L}$)	Single analyst precision, s_r' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Benzene	$0.92C+0.57$	$0.09\bar{x}+0.59$	$0.21\bar{x}+0.56$
Chlorobenzene	$0.95C+0.02$	$0.09\bar{x}+0.23$	$0.17\bar{x}+0.10$
1,2-Dichlorobenzene	$0.93C+0.52$	$0.17\bar{x}-0.04$	$0.22\bar{x}+0.53$
1,3-Dichlorobenzene	$0.96C-0.04$	$0.15\bar{x}-0.10$	$0.19\bar{x}+0.09$
1,4-Dichlorobenzene	$0.93C-0.09$	$0.15\bar{x}+0.28$	$0.20\bar{x}+0.41$
Ethylbenzene	$0.94C+0.31$	$0.17\bar{x}+0.46$	$0.26\bar{x}+0.23$
Toluene	$0.94C+0.65$	$0.09\bar{x}+0.48$	$0.18\bar{x}+0.71$

x' = Expected recovery for one or more measurements of a sample containing concentration C , in $\mu\text{g/L}$.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of \bar{x} , in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{x} , in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

\bar{x} = Average recovery found for measurements of samples containing a concentration of C , in $\mu\text{g/L}$.

Figure 1
Chromatogram of Aromatic Volatile Organics
(column 1 conditions)

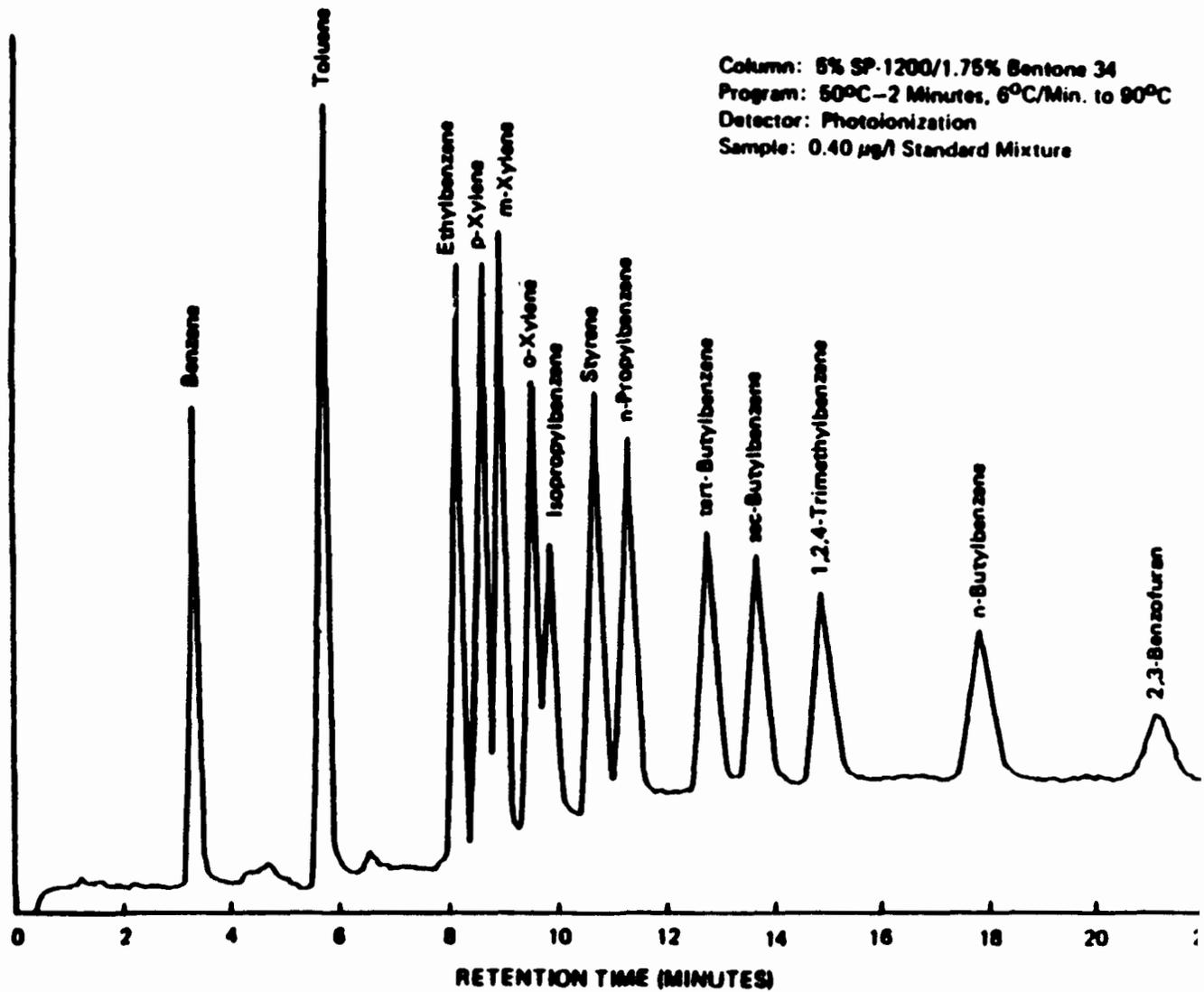
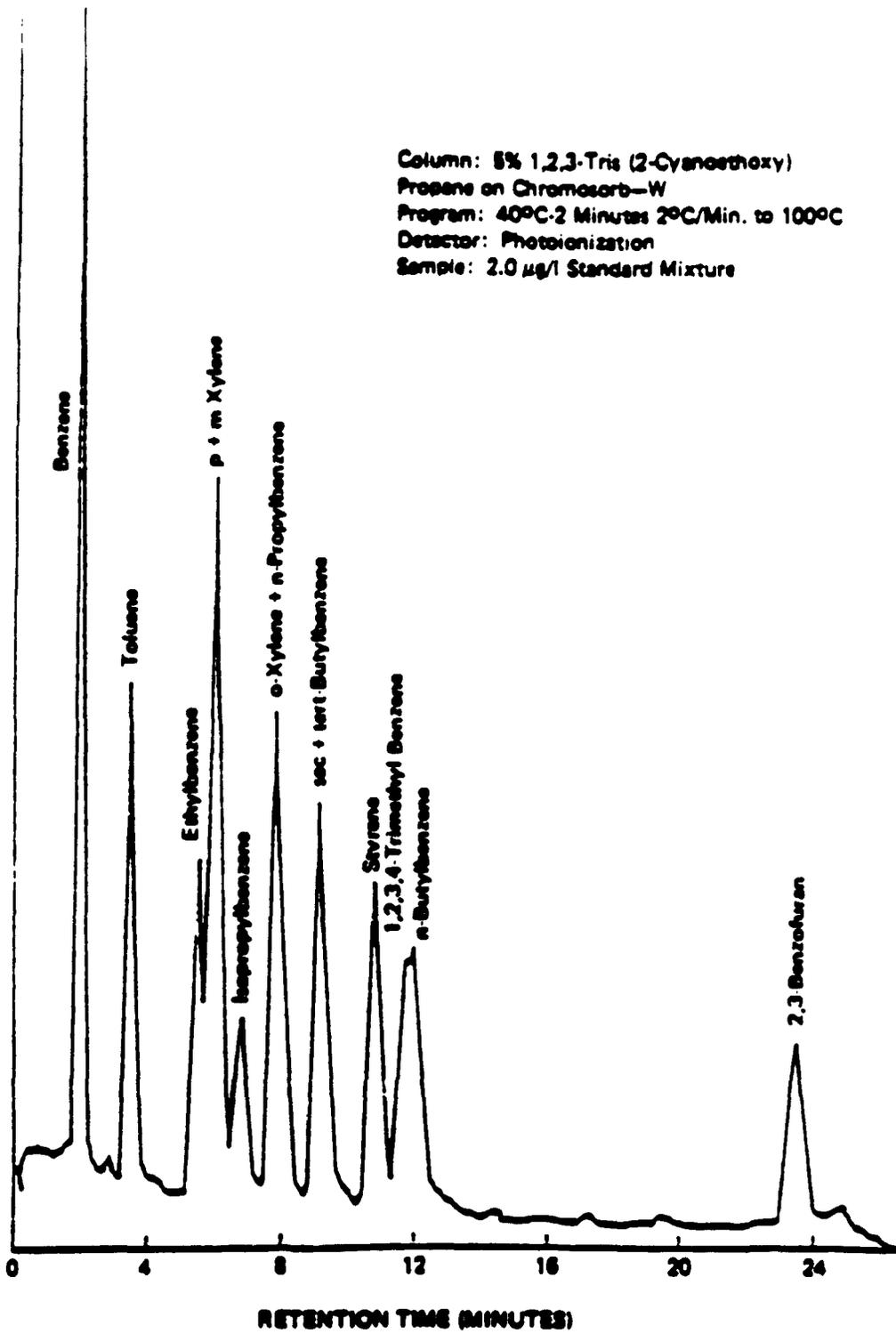
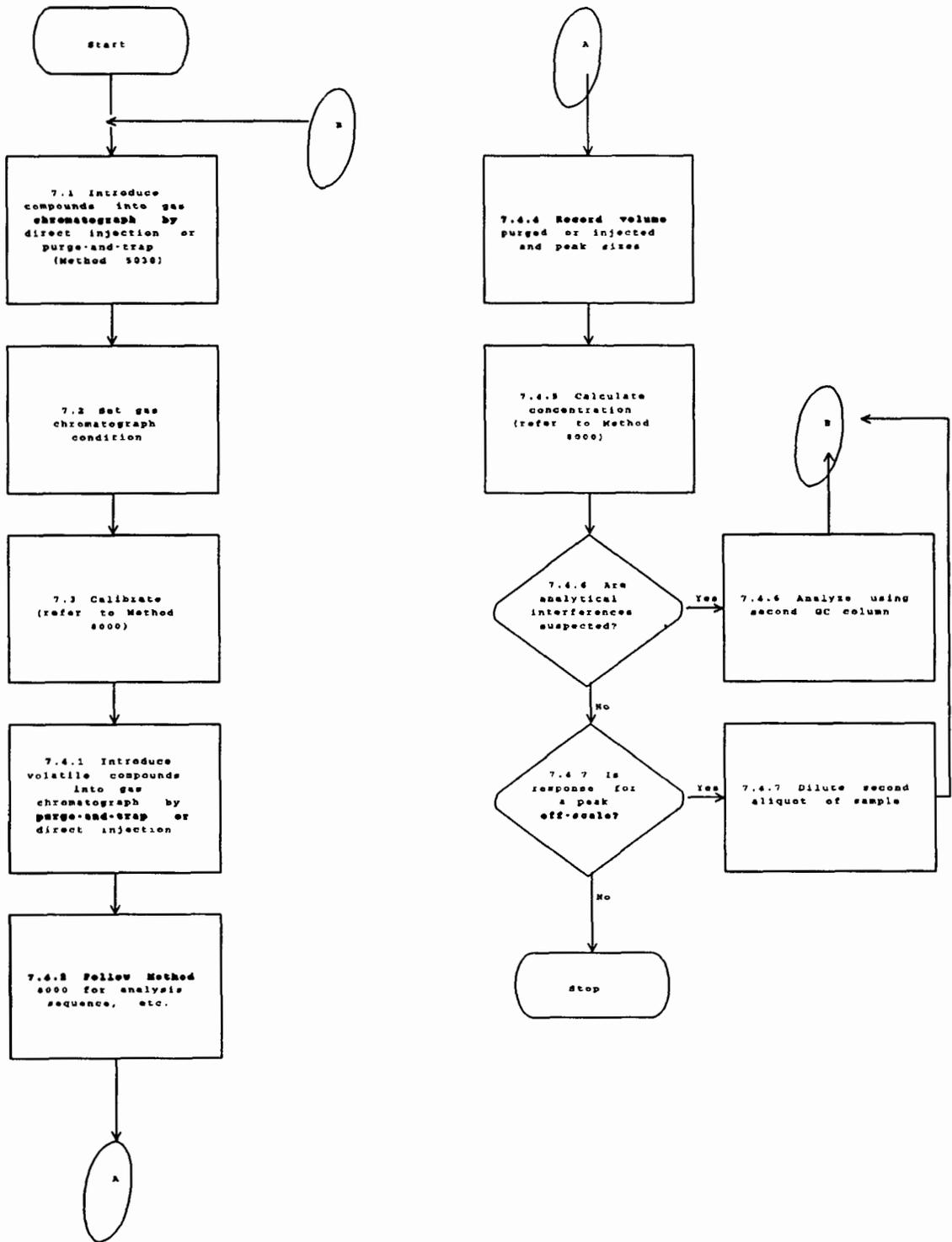


Figure 2
Chromatogram of Aromatic Volatile Organics
(column 2 conditions)



METHOD 8020A
 AROMATIC VOLATILE ORGANICS BY GAS CHROMATOGRAPHY



METHOD 8021A

HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING
PHOTOIONIZATION AND ELECTROLYTIC CONDUCTIVITY DETECTORS
IN SERIES: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8021 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

Analyte	CAS No. ^a	Appropriate Technique	
		Purge-and-Trap	Direct Injection
Benzene	71-43-2	b	b
Bromobenzene	108-86-1	b	b
Bromochloromethane	74-97-5	b	b
Bromodichloromethane	75-27-4	b	b
Bromoform	75-25-2	b	b
Bromomethane	74-83-9	b	b
n-Butylbenzene	104-51-8	b	b
sec-Butylbenzene	135-98-8	b	b
tert-Butylbenzene	98-06-6	b	b
Carbon tetrachloride	56-23-5	b	b
Chlorobenzene	108-90-7	b	b
Chlorodibromomethane	124-48-1	b	b
Chloroethane	75-00-3	b	b
Chloroform	67-66-3	b	b
Chloromethane	74-87-3	b	b
2-Chlorotoluene	95-49-8	b	b
4-Chlorotoluene	106-43-4	b	b
1,2-Dibromo-3-chloropropane	96-12-8	pp	b
1,2-Dibromoethane	106-93-4	b	b
Dibromomethane	74-95-3	b	b
1,2-Dichlorobenzene	95-50-1	b	b
1,3-Dichlorobenzene	541-73-1	b	b
1,4-Dichlorobenzene	106-46-7	b	b
Dichlorodifluoromethane	75-71-8	b	b
1,1-Dichloroethane	75-34-3	b	b
1,2-Dichloroethane	107-06-2	b	b
1,1-Dichloroethene	75-35-4	b	b
cis-1,2-Dichloroethene	156-59-4	b	b
trans-1,2-Dichloroethene	156-60-5	b	b

Analyte	CAS No. ^a	Appropriate Technique	
		Purge-and-Trap	Direct Injection
1,2-Dichloropropane	78-87-5	b	b
1,3-Dichloropropane	142-28-9	b	b
2,2-Dichloropropane	590-20-7	b	b
1,1-Dichloropropene	563-58-6	b	b
cis-1,3-dichloropropene	10061-01-5	b	b
trans-1,3-dichloropropene	10061-02-6	b	b
Ethylbenzene	100-41-4	b	b
Hexachlorobutadiene	87-68-3	b	b
Isopropylbenzene	98-82-8	b	b
p-Isopropyltoluene	99-87-6	b	b
Methylene chloride	75-09-2	b	b
Naphthalene	91-20-3	b	b
n-Propylbenzene	103-65-1	b	b
Styrene	100-42-5	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b
Tetrachloroethene	127-18-4	b	b
Toluene	108-88-3	b	b
1,2,3-Trichlorobenzene	87-61-6	b	b
1,2,4-Trichlorobenzene	120-82-1	b	b
1,1,1-Trichloroethane	71-55-6	b	b
1,1,2-Trichloroethane	79-00-5	b	b
Trichloroethene	79-01-6	b	b
Trichlorofluoromethane	75-69-4	b	b
1,2,3-Trichloropropane	96-18-4	b	b
1,2,4-Trimethylbenzene	95-63-6	b	b
1,3,5-Trimethylbenzene	108-67-8	b	b
Vinyl chloride	75-01-4	b	b
o-Xylene	95-47-6	b	b
m-Xylene	108-38-3	b	b
p-Xylene	106-42-3	b	b

- a Chemical Abstract Services Registry Number.
b Adequate response by this technique.
pp Poor purging efficiency resulting in high EQLs.
i Inappropriate technique for this analyte.
pc Poor chromatographic behavior.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e. xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021A for an individual compound is approximately 1 $\mu\text{g}/\text{kg}$ (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 $\mu\text{g}/\text{L}$ for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is recommended for use only by analysts experienced in the measurement of purgeable organics at the low $\mu\text{g}/\text{L}$ level or by experienced technicians under the close supervision of a qualified analyst.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (references 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachloro-butadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030 (where applicable). A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series.

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from

organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.3 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Column - 60 m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5 μm film thickness (Supelco Inc., or equivalent).

4.2.2 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.3 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends (Teflon or Kel-F).

4.5 Microsyringe - 25 μL with a 2 in. x 0.006 in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10, 100 μL .

4.7 Syringes - 0.5, 1.0, and 5 mL, gas tight with shut-off valve.

4.8 Bottles - 15 mL, Teflon lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Refrigerator.

4.11 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades

may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH₃OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store away from other solvents.

5.4 Vinyl chloride, (99.9% pure), CH₂=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

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

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 Liquids: Using a 100 μL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5 mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a Hamilton Lecture Bottle Septum (#86600). Attach Teflon tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to

calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

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

5.5.5 Prepare fresh stock standards every two months for gases. Reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently. All other standards must be replaced after six months. Both gas and liquid standards must be monitored closely by comparison to the initial calibration curve and by comparison to QC reference samples. It may be necessary to replace the standards more frequently if either check exceeds a 25% difference.

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 5.7 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.7 Calibration standards, at a *minimum* of five concentration levels are prepared in organic-free reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of the concentrations found in real samples or should define the working range of the GC. Standards (one or more) should contain each analyte for detection by this method (e.g. some or all of the target analytes may be included). In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.7.1 Do not inject more than 20 μL of alcoholic standards into 100 mL of water.

5.7.2 Use a 25 μL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.7.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.7.4 Mix aqueous standards by inverting the flask three times.

5.7.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.7.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.7.7 Aqueous standards are not stable and should be discarded after one hour, unless properly sealed and stored. The aqueous standards can be stored up to 12 hours, if held in sealed vials with zero headspace.

5.8 Internal standards - Prepare a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol, using the procedures described in Sections 5.5 and 5.6. It is recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10 μ L of such a standard to 5.0 mL of sample or calibration standard would be equivalent to 10 μ g/L.

5.9 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of bromochloromethane, 2-bromo-1-chloropropane, 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.5, add a volume to give 750 μ g of each surrogate to 45 mL of organic-free reagent water contained in a 50 mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/ μ L. Add 10 μ L of this surrogate spiking solution directly into the 5 mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Section 5.8).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-concentration contaminated soils and sediments. For medium-concentration soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD).

7.2.2 Oven settings:

Carrier gas (Helium) Flow rate: 6 mL/min.

Temperature program

Initial temperature: 10°C, hold for 8 minutes at
Program: 10°C to 180°C at 4°C/min
Final temperature: 180°C, hold until all expected
compounds have eluted.

7.2.3 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.4 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

Reactor tube:	Nickel, 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-Propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

7.2.5 A sample chromatogram obtained with this column is presented in Figure 5. This column was used to develop the method performance statements in Section 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Section 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Section 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method (see Section 7.4.1.1). If the internal standard calibration technique is used, add 10 μ L of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes) direct injection of the sample into the GC system with a 10 μ L syringe may be appropriate. The

detection limit is very high (approximately 10,000 $\mu\text{g/L}$), therefore, it is only permitted where concentrations in excess of 10,000 $\mu\text{g/L}$ are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using a second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Quality control required to validate the GC system operation is found in Method 8000.

8.2.1 The quality control reference sample (Method 8000) should contain each parameter of interest at a concentration of 10 mg/L in methanol.

8.2.2 Table 2 gives method accuracy and precision as functions of concentration for the analytes of interest.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.

- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1 $\mu\text{g/L}$. These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10 $\mu\text{g/L}$. Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

10.0 REFERENCES

1. Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series, Method 502.2; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, September, 1986.
2. The Determination of Halogenated Chemicals in Water by the Purge and Trap Method, Method 502.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio 45268, September, 1986.
3. Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography, Method 503.1; Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, September, 1986.
4. Glaser, J.A.; Forest, D.L.; McKee, G.D.; Quave, S.A.; Budde, W.L. "Trace Analyses for Wastewaters"; Environ. Sci. Technol. 1981, 15, 1426.
5. Bellar, T.A.; Lichtenberg, J.J. The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, Ohio, 45268.

TABLE 1.

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR
VOLATILE ORGANIC COMPOUNDS ON PHOTOIONIZATION DETECTION (PID) AND
HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time ^a minute	HECD Ret. Time minute	PID MDL μg/L	HECD MDL μg/L
Dichlorodifluoromethane	- ^b	8.47		0.05
Chloromethane	-	9.47		0.03
Vinyl Chloride	9.88	9.93	0.02	0.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND ^c	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethylbenzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropylbenzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

TABLE 1.
(Continued)

Analyte	PID Ret. Time ^a minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
n-Propylbenzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethylbenzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butylbenzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

^a Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

^b Dash (-) indicates detector does not respond.

^c ND = Not determined.

TABLE 2.
SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER^d

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, ^a %	Standard Deviation of Recovery	Recovery, ^a %	Standard Deviation of Recovery
Benzene	99	1.2	- ^b	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
m-Butylbenzene	97	2.6	-	-
p-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
o-Chlorotoluene	ND ^c	ND	97	2.6
p-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Bromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Bromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
1,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
o-Tolylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2.
(Continued)

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Recovery, ^a %	Standard Deviation of Recovery	Recovery, ^a %	Standard Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	-
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

^a Recoveries and standard deviations were determined from seven samples and spiked a 10 µg/L of each analyte. Recoveries were determined by internal standard method. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

^b Detector does not respond.

^c ND = Not determined.

^d This method was tested in a single laboratory using water spiked at 10 µg/L (see reference 8).

TABLE 3.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL)
FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

^a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

^b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

FIGURE 1.
PURGING DEVICE

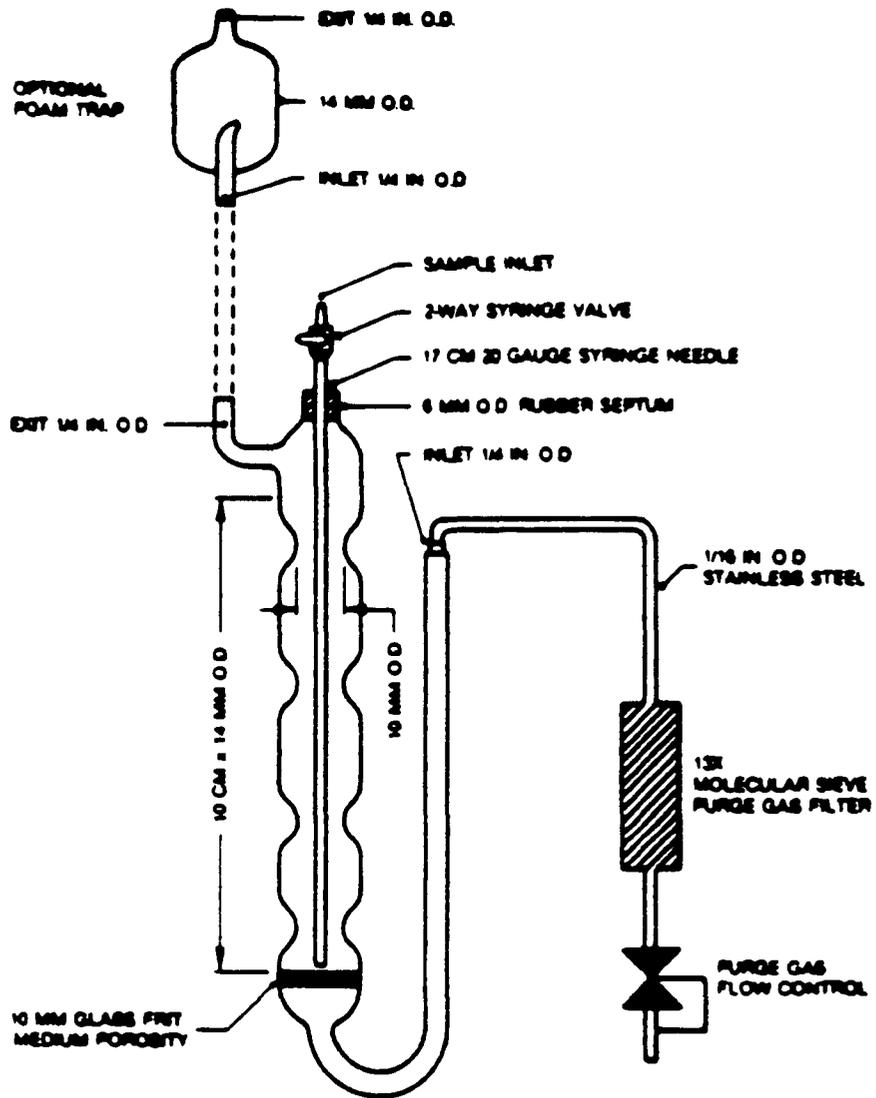


FIGURE 2.
TRAP PACKINGS AND CONSTRUCTION TO INCLUDE DESORB CAPABILITY

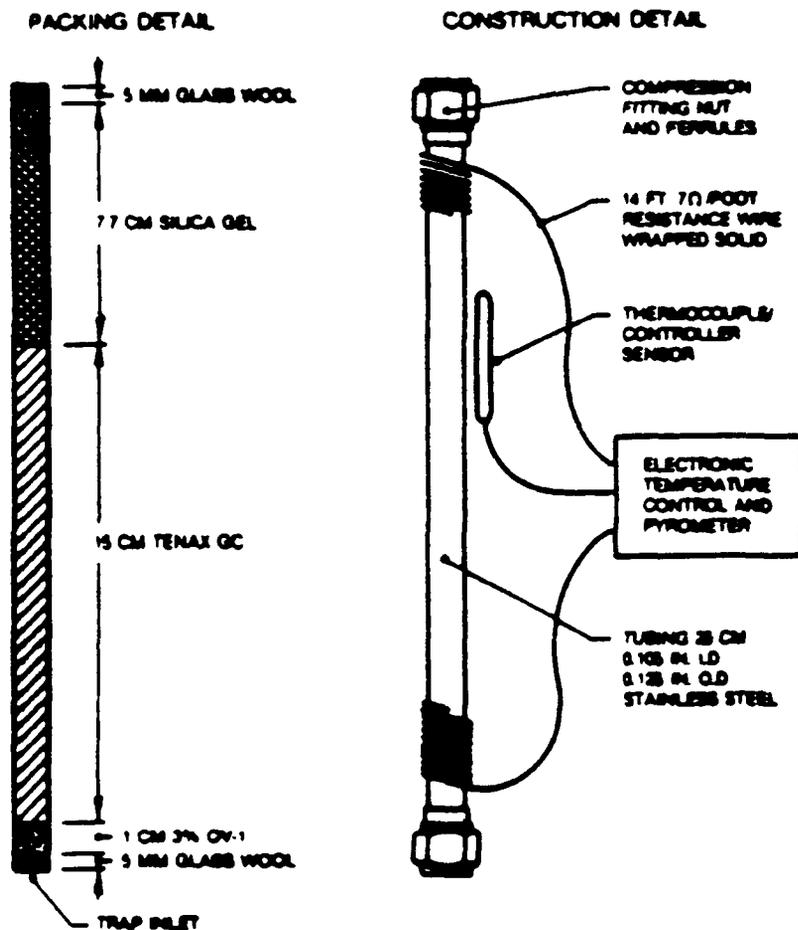


FIGURE 3.
PURGE-AND-TRAP SYSTEM - PURGE MODE

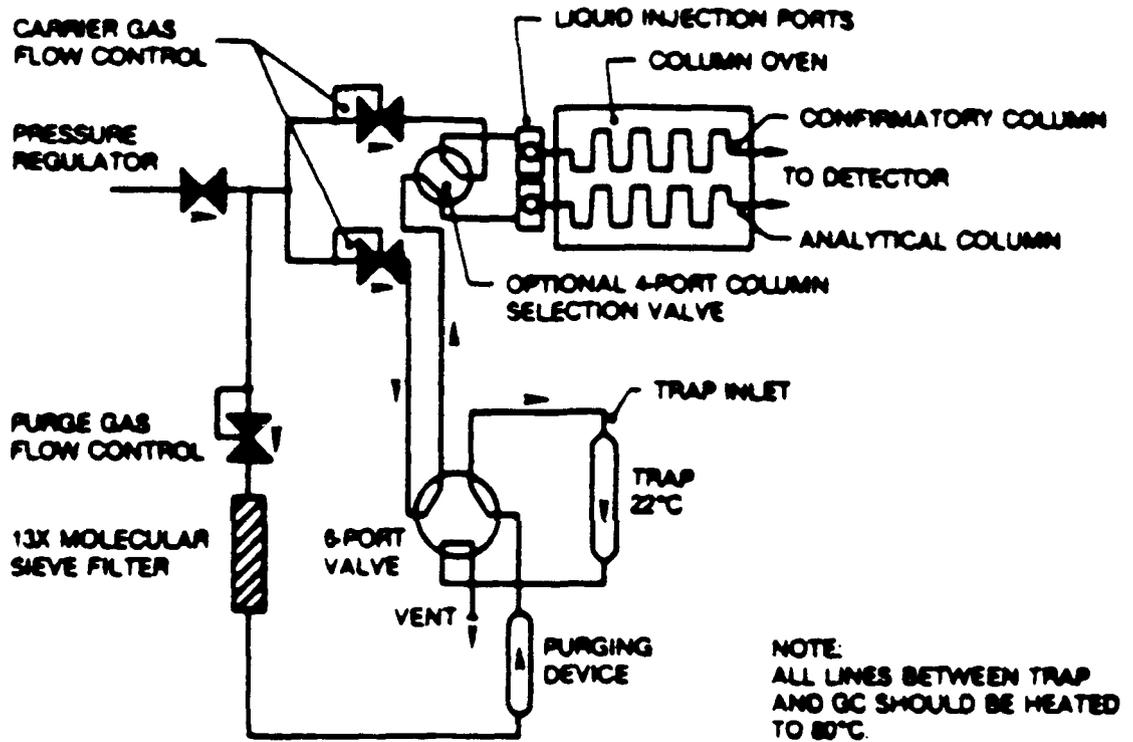


FIGURE 4.
SCHEMATIC OF PURGE-AND-TRAP DEVICE - DESORB MODE

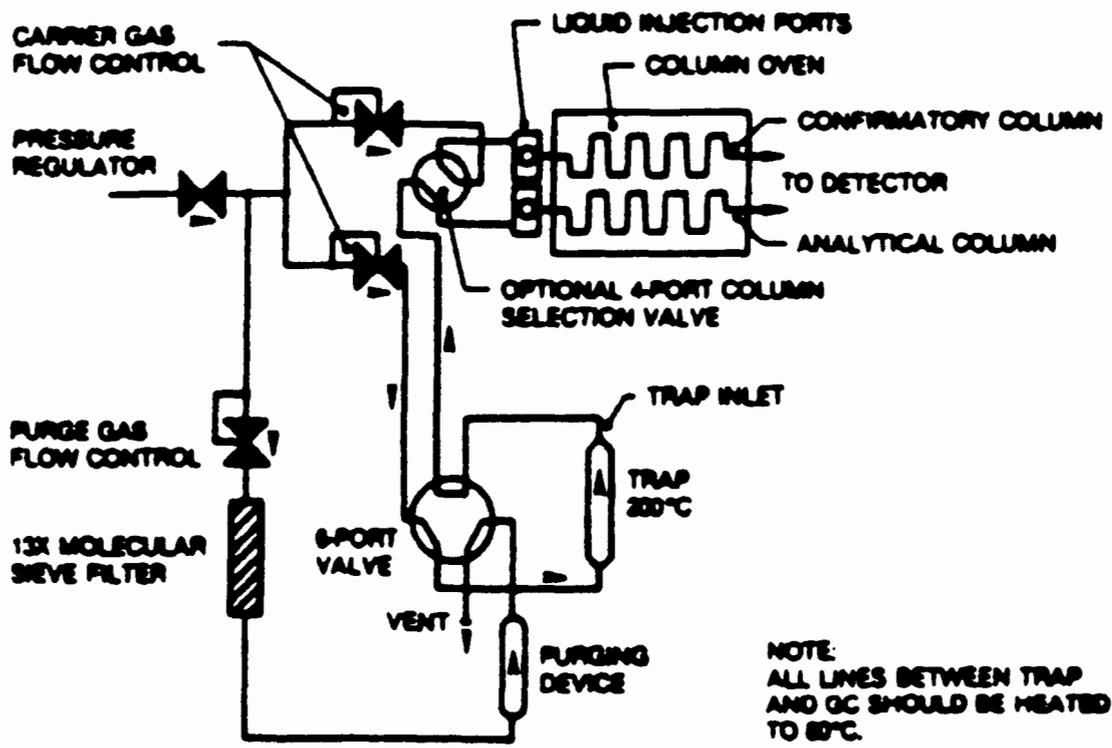
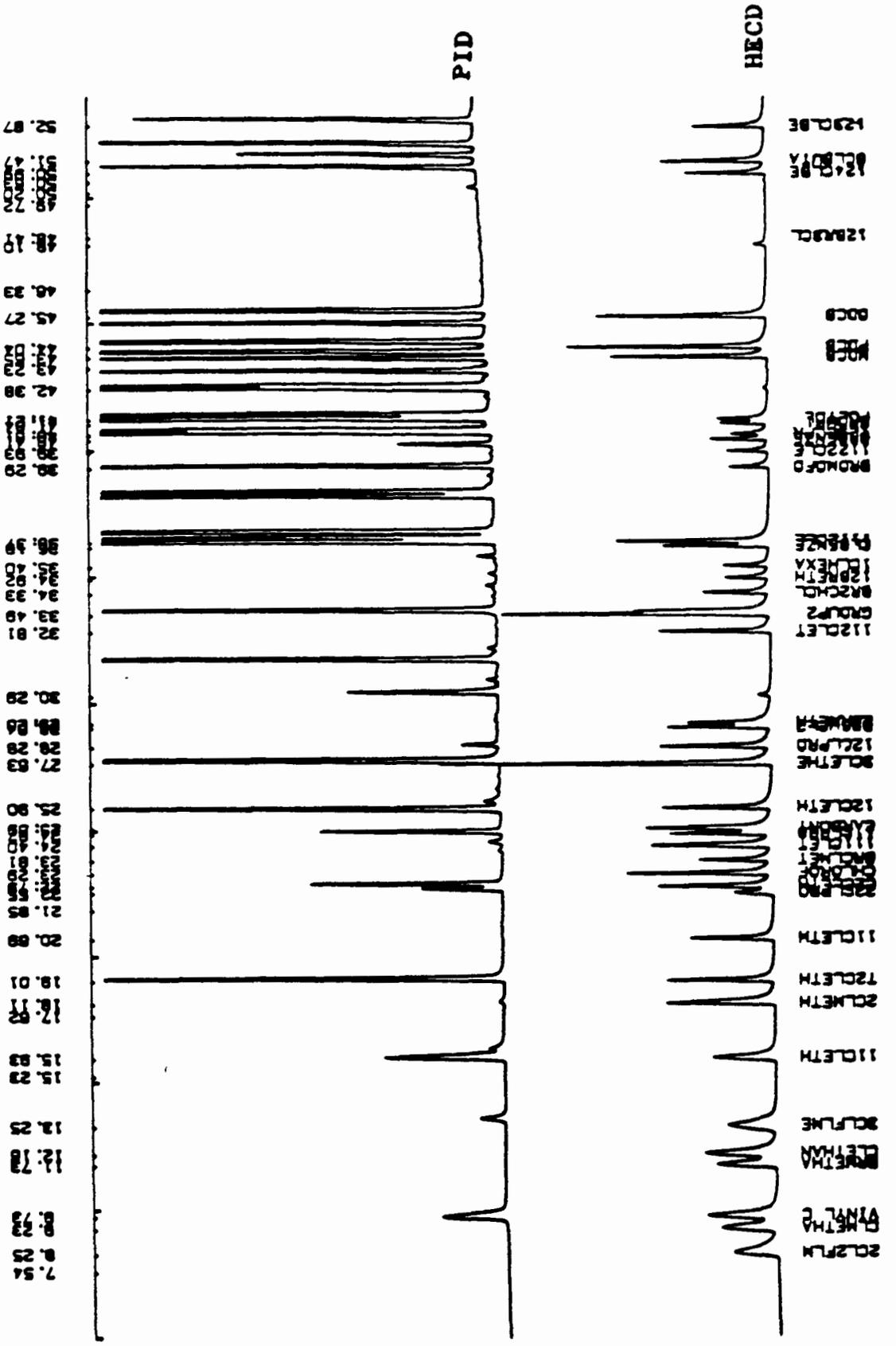


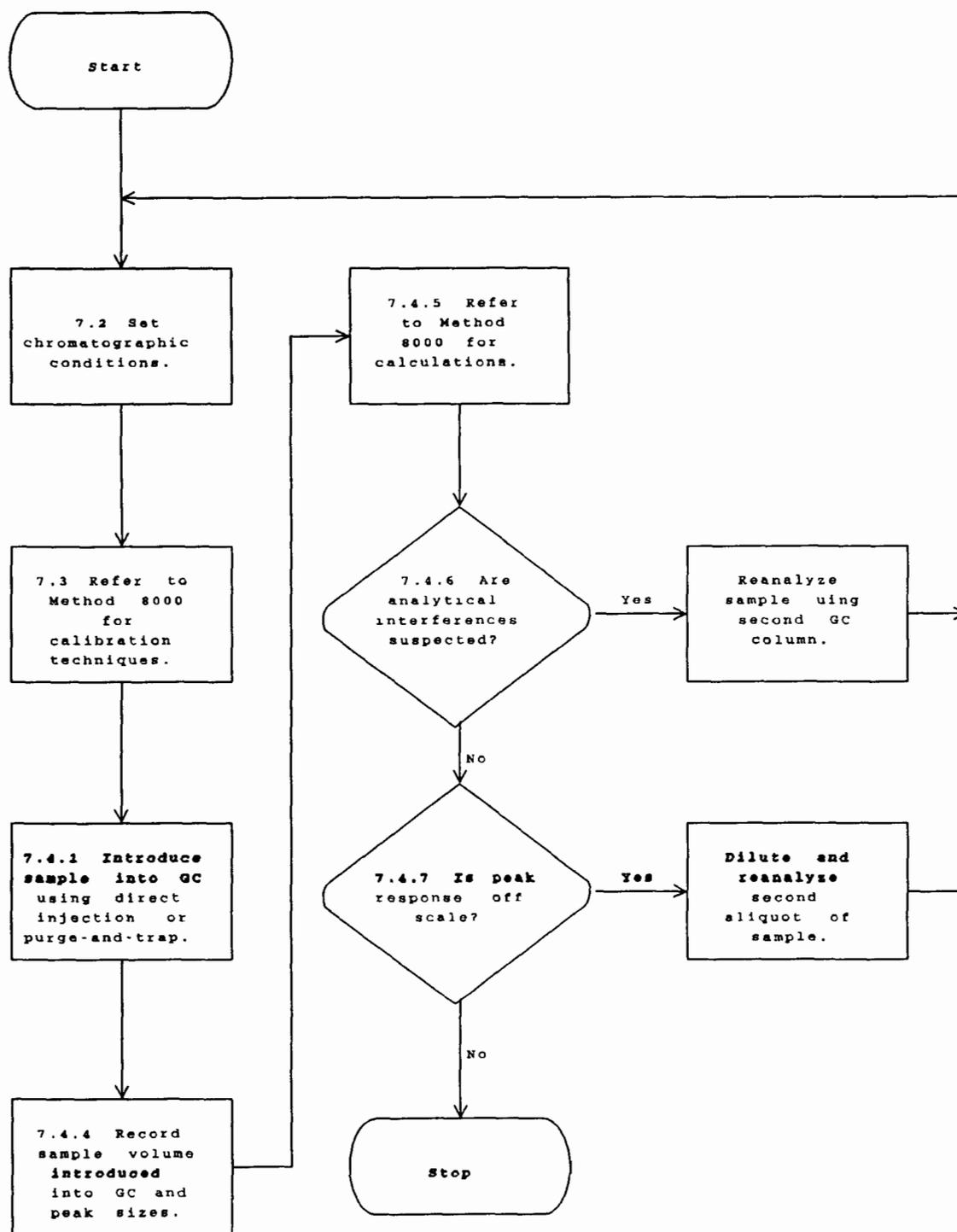
FIGURE 5.
GAS CHROMATOGRAM OF VOLATILE ORGANICS

COLUMN: 60 METER X 0.75 MM I.D. VOCOL CAPILLARY

PURGE AND TRAP VOC'S WITH MALL & PID IN SERIES



METHOD 8021A
HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION
AND ELECTROLYTIC CONDUCTIVITY DETECTORS IN SERIES:
CAPILLARY COLUMN TECHNIQUE



METHOD 8030

ACROLEIN, ACRYLONITRILE, ACETONITRILE

1.0 SCOPE AND APPLICATION

1.1 Method 8030 is used to determine the concentration of the following three volatile organic compounds:

Acrolein (Propenal)
Acrylonitrile
Acetonitrile

1.2 Table 1 lists chromatographic conditions and method detection limits for acrolein and acrylonitrile in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8030 provides gas chromatographic conditions for the detection of the three volatile organic compounds. Samples can be analyzed using direct injection or purge-and-trap (Method 5030). Ground water samples must be analyzed using Method 5030. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a flame ionization detector (FID).

2.2 The method provides an optional gas chromatographic column that may be helpful in resolving the analytes from interferences that may occur and for analyte confirmation.

3.0 INTERFERENCES

3.1 Refer to Methods 5030 and 8000.

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections or purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak height and/or peak area is recommended.

4.1.2 Columns

4.1.2.1 Column 1 - 10 ft x 2 mm i.d. stainless steel or glass packed with Porapak-QS (80/100 mesh) or equivalent.

4.1.2.2 Column 2 - 6 ft x 0.1 in i.d. stainless steel or glass packed with Chromosorb 101 (60/80 mesh) or equivalent.

4.1.3 Detector - Flame ionization (FID).

4.2 Sample introduction apparatus - Refer to Method 5030 for the appropriate equipment for sample introduction purposes.

4.3 Syringes - A 5-mL Luerlok glass hypodermic and a 5-mL, gas-tight with shutoff valve.

4.4 Volumetric flasks - 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringes - 10- and 25- μ L with a 0.006 in i.d. needle (Hamilton 702N or equivalent) and a 100- μ L.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Stock standards - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in water using assayed liquids. Because acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood.

5.3.1 Place about 9.8 mL of water in a 10-mL tared ground-glass-stoppered volumetric flask. For acrolein standards the water must be adjusted to pH 4-5 using hydrochloric acid (1:1) or sodium hydroxide (10N), if necessary. Weigh the flask to the nearest 0.1 mg.

5.3.2 Using a 100- μ L syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the water without contacting the neck of the flask.

5.3.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (μ g/ μ L) from the net gain in weight. When compound purity is

assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.3.4 Transfer the stock standard solution into a bottle with a Teflon lined screw-cap. Store, with minimal headspace, at 4°C and protect from light.

5.3.5 Prepare fresh standards daily.

5.4 Secondary dilution standards - Using stock standard solutions, prepare in water secondary dilution standards, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Step 5.5 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.5 Calibration standards - Calibration standards at a minimum of five concentration levels are prepared in water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Each standard should contain each analyte for detection by this method. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

5.5.1 Use a 25- μ L Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of standards into water).

5.5.2 Never use pipets to dilute or transfer samples or aqueous standards.

5.5.3 These standards must be prepared daily.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Step 5.5.

5.6.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Steps 5.3 and 5.4. It is recommended that the secondary dilution standard be prepared at a concentration of 15 ug/mL of each internal standard compound. The addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be equivalent to 30 ug/L.

5.6.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.7 Surrogate standards - The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds (e.g. compounds similar in analytical behavior to the analytes of interest but which are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Step 5.3, add a volume to give 750 ug of each surrogate to 45 mL of water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/uL. Add 10 uL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Step 5.6.2).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection or purge-and-trap (Method 5030). Method 5030 may be used directly on ground water samples or low-level contaminated soils and sediments. For high-level soils or sediments, methanolic extraction, as described in Method 5030, may be necessary prior to purge-and-trap analysis.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Column 1 - Set helium gas flow at 30 mL/min flow rate. Set column temperature at 110°C for 1.5 minutes; then heat as rapidly as possible to 150°C and hold for 20 minutes.

7.2.2 Column 2 - Set helium gas flow at 40 mL/min flow rate. Set column temperature at 80°C for 4 minutes; then program at 50°C/min to 120°C and hold for 12 minutes.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Step 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Method 5030 (purge-and-trap method) or the direct injection method. If the internal standard calibration technique is used, add 10 μL of the internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g. aqueous process wastes), direct injection of the sample into the GC system with a 10 μL syringe may be appropriate. The detection limit is very high (approximately 10,000 $\mu\text{g/L}$); therefore, it is only permitted when concentrations in excess of 10,000 $\mu\text{g/L}$ are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.2 Follow Step 7.6 of Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times and detection limits for a number of organic compounds analyzable using this method. Figure 1 illustrates the chromatographic separation of acrolein and of acrylonitrile using Column 1.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Step 7.8 of Method 8000.

7.4.6 If analytical interferences are suspected, or for the purpose of confirmation, analysis using the second GC column is recommended.

7.4.7 If the response for a peak is off-scale, prepare a dilution of the sample with water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 8000 for gas chromatographic procedures. Quality control to ensure the proper operation of the purge-and-trap device is covered in Method 5030.

8.2 Procedures to check the GC system operation are found in Method 8000, Step 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Step 8.6) should contain each parameter of interest at a concentration of 25 ug/mL in water.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives single laboratory accuracy and precision for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, the average recoveries and standard deviations presented in Table 4 were obtained using Method 5030. Seven replicate samples were analyzed at each spike level.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and by the calibration procedure used.

10.0 REFERENCES

1. Bellar, T.A. and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), pp. 739-744, 1974.
2. Bellar, T.A. and J.J. Lichtenberg, "Semi-Automated Headspace Analysis of Drinking Waters and Industrial Waters for Purgeable Volatile Organic Compounds," in Van Hall, ed., Measurement of Organic Pollutants in Water and Wastewater, ASTM STP 686, pp. 108-129, 1979.
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, J., et al., Environmental Monitoring Near Industrial Sites - Acrylonitrile, Office of Toxic Substances, U.S. EPA, Washington, DC, EPA 560/6-79-003, 1979.

5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.
6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.
7. Kerns, E.H., et al. "Determination of Acrolein and Acrylonitrile in Water by Heated Purge and Trap Technique," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, 1980.
8. "Evaluation of Method 603," Final Report for EPA Contract 68-03-1760 (in preparation).
9. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
10. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Compound	Retention time (min)		Method detection limit ^a (ug/L)
	Col. 1	Col. 2	
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

^aBased on using purge-and-trap, Method 5030.

TABLE 2.
DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-level soil	10
Water miscible liquid waste	500
High-level soil and sludge	1250
Non-water miscible waste	1250

^a Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

^b PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
CALIBRATION AND QC ACCEPTANCE CRITERIA^a

Parameter	Range for Q (ug/L)	Limit for S (ug/L)	Range for \bar{x} (ug/L)	Range P, P _S (%)
Acrolein	45.9-54.1	4.6	42.9-60.1	88-118
Acrylonitrile	41.2-58.8	9.9	33.1-69.9	71-135

Q = Concentration measured in QC check sample, in ug/L.
 S = Standard deviation of four recovery measurements, in ug/L.
 \bar{x} = Average recovery for four recovery measurements, in ug/L.
 P, P_S = Percent recovery measured.

^a Criteria from 40 CFR Part 136 for Method 603 and were calculated assuming a QC check sample concentration of 50 ug/L.

TABLE 4.
SINGLE LABORATORY ACCURACY AND PRECISION

Parameter	Spike conc. (ug/L)	Average recovery (ug/L)	Standard deviation (ug/L)	Average percent recovery	Sample matrix ^a
Acrolein	5.0	5.2	0.2	104	AW
	50.0	51.4	0.7	103	AW
	5.0	4.0	0.2	80	POTW
	50.0	44.4	0.8	89	POTW
	5.0	0.1	0.1	2	IW
Acrylonitrile	100.0	9.3	1.1	9	IW
	5.0	4.2	0.2	84	AW
	50.0	51.4	1.5	103	AW
	20.0	20.1	0.8	100	POTW
	100.0	101.3	1.5	101	POTW
	10.0	9.1	0.8	91	IW
	100.0	104.0	3.2	104	IW

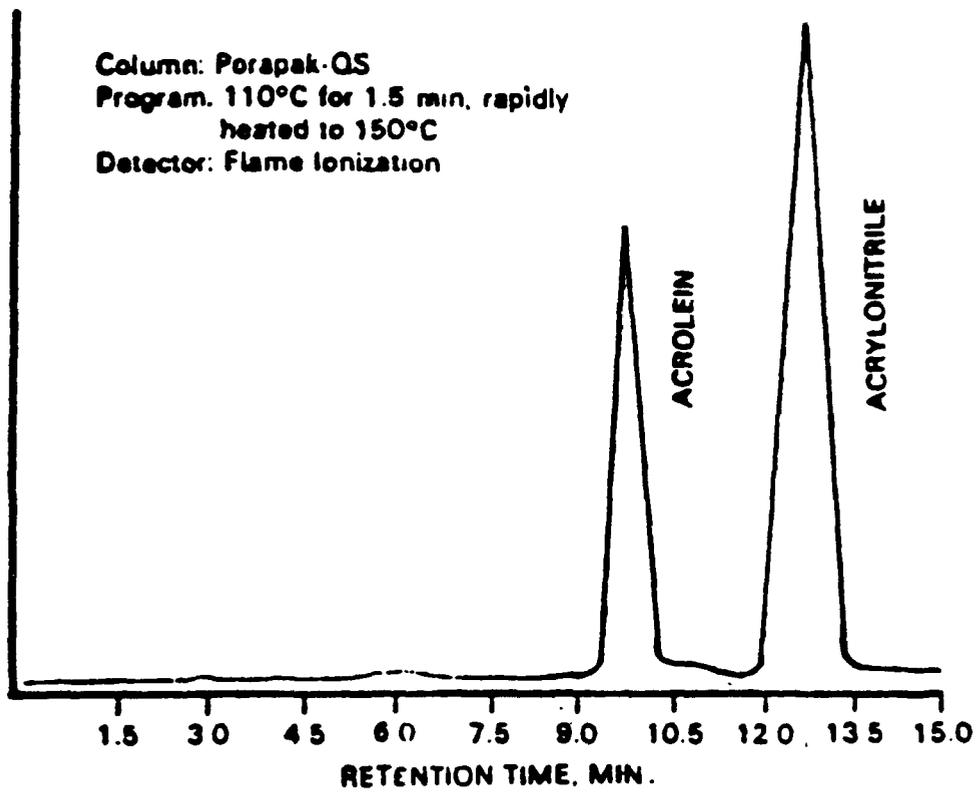
^aAW = ASTM Type II water.

POTW = Prechlorination secondary effluent from a municipal sewage treatment plant.

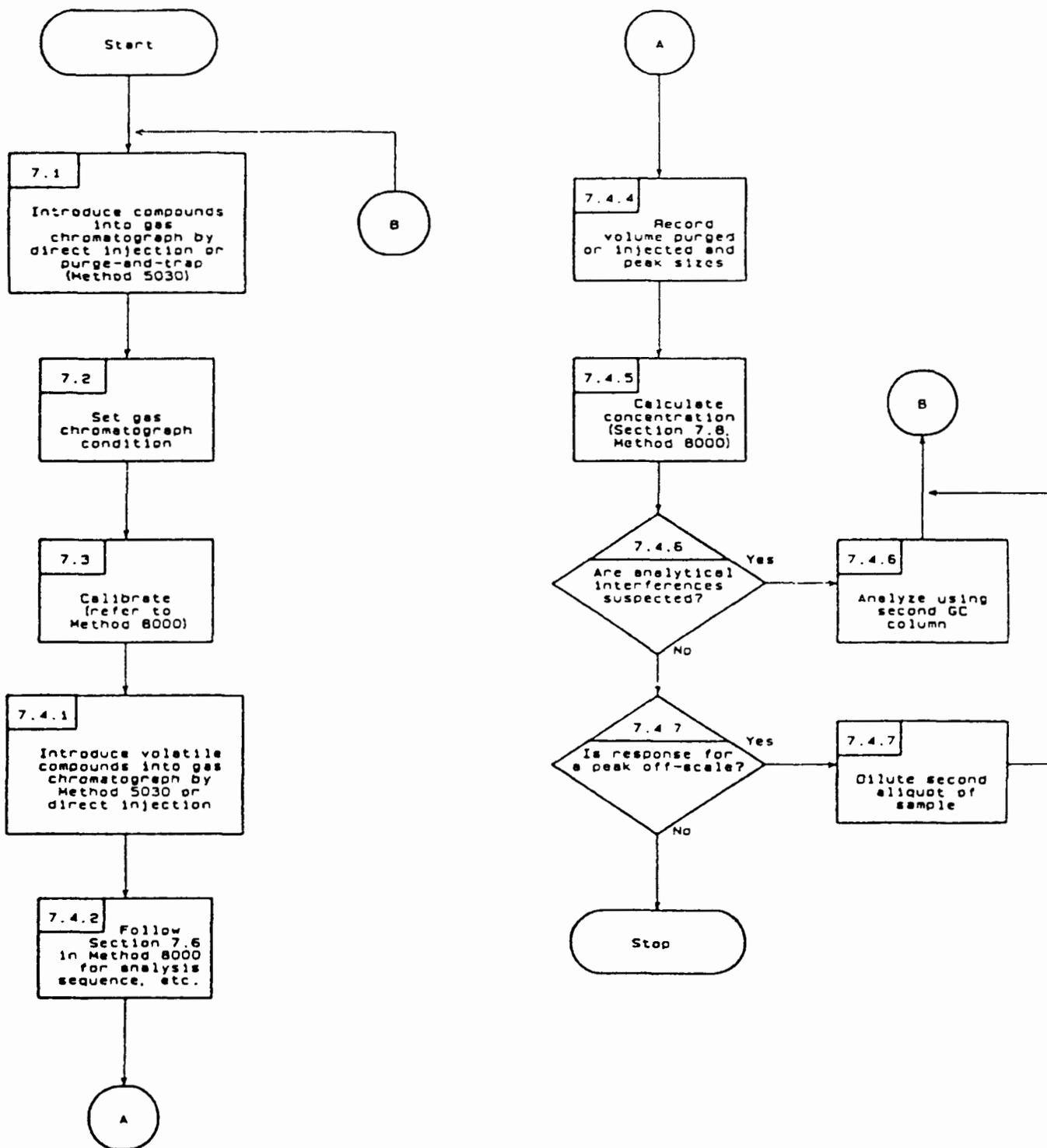
IW = Industrial wastewater containing an unidentified acrolein reactant.

Figure 1.

Gas chromatogram of acrolein and acrylonitrile.



METHOD 8030
ACROLEIN, ACRYLONITRILE, ACETONITRILE



METHOD 8031

ACRYLONITRILE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8031 is used to determine the concentration of acrylonitrile in water. This method may also be applicable to other matrices. The following compounds can be determined by this method:

Compound Name	CAS No. ^a
Acrylonitrile	107-13-1

^a Chemical Abstract Services Registry Number.

1.2 The estimated quantitation limit of Method 8031 for determining the concentration of acrylonitrile in water is approximately 10 µg/L.

1.3 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured sample volume is micro-extracted with methyl tert-butyl ether. The extract is separated by gas chromatography and measured with a Nitrogen/Phosphorus detector.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that leads to discrete artifacts and/or elevated baselines in gas chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks.

3.2 Samples can be contaminated by diffusion of volatile organics around the septum seal into the sample during handling and storage. A field blank should be prepared from organic-free reagent water and carried through the sampling and sample handling protocol to serve as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an

unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph system

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: Porapak Q - 6 ft., 80/10 Mesh, glass column, or equivalent.

4.1.3 Nitrogen/Phosphorus detector.

4.2 Materials

4.2.1 Grab sample bottles - 40 mL VOA bottles.

4.2.2 Mixing bottles - 90 mL bottle with a Teflon lined cap.

4.2.3 Syringes - 10 μ L and 50 μ L.

4.2.4 Volumetric flask (Class A) - 100 mL.

4.2.5 Graduated cylinder - 50 mL.

4.2.6 Pipet (Class A) - 5, 15, and 50 mL.

4.2.7 Vials - 10 mL.

4.3 Preparation

4.3.1 Prepare all materials to be used as described in Chapter 4 for volatile organics.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 General

5.2.1 Methanol, CH₃OH - Pesticide quality, or equivalent.

5.2.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2.3 Methyl tert-butyl ether, $\text{CH}_3\text{O}t\text{-C}_4\text{H}_9$ - Pesticide quality, or equivalent.

5.2.4 Acrylonitrile, $\text{H}_2\text{C}:\text{CHCN}$, 98%.

5.3 Stock standard solution

5.3.1 Stock standard solutions - Can be prepared from pure standard materials or can be purchased as certified solutions. Commercially prepared stock standards can be used if they are verified against EPA standards. If EPA standards are not available for verification, then standards certified by the manufacturer and verified against a standard made from pure material is acceptable.

5.3.2 The stock standard solution may be prepared by volume or by weight. Stock solutions must be replaced after one year, or sooner if comparison with the check standards indicates a problem.

CAUTION: Acrylonitrile is toxic. Standard preparation should be performed in a laboratory fume hood.

5.3.2.1 To prepare the stock standard solution by volume: inject 10 μL of acrylonitrile (98%) into a 100 mL volumetric flask with a syringe. Make up to volume with methanol.

5.3.2.2 To prepare the stock standard solution by weight: Place about 9.8 mL of organic-free reagent water into a 10 mL volumetric flask before weighing the flask and stopper. Weigh the flask and record the weight to the nearest 0.0001 g. Add two drops of pure acrylonitrile, using a 50 μL syringe, to the flask. The liquid must fall directly into the water, without contacting the inside wall of the flask. Stopper the flask and then reweigh. Dilute to volume with organic-free reagent water. Calculate the concentration from the net gain in weight.

5.4 Working standard solutions

5.4.1 Prepare a minimum of 5 working standard solutions that cover the range of analyte concentrations expected in the samples. Working standards of 20, 40, 60, 80, and 100 $\mu\text{g}/\text{L}$ may be prepared by injecting 10, 20, 30, 40, and 50 μL of the stock standard solution prepared in Section 5.3.2.1 into 5 separate 90 mL mixing bottles containing 40 mL of organic-free reagent water.

5.4.2 Inject 15 mL of methyl tert-butyl ether into each mixing bottle, shake vigorously, and let stand 5 minutes, or until layers have separated.

5.4.3 Remove 5 mL of top layer by pipet, and place in a 10 mL vial.

5.4.4 Keep all standard solutions below 4°C until used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Sample Extraction

7.1.1 Pour 40 mL of the sample into a 90 mL mixing bottle. Pipet 15 mL of Methyl tert-butyl ether into the mixing bottle. Shake vigorously for about 2 min. and let stand for about 5 min. Remove about 5 mL of the top layer and store in a 10 mL vial.

7.2 Chromatographic Conditions (Recommended)

Carrier Gas (He) flow rate: 35 mL/min.
Column Temperature: 180° C, Isothermal
Injection port temperature: 250° C
Detector temperature: 250° C
Detector Current (DC): 18 volts
Gases: Hydrogen, 3 mL/min; Air, 290 mL/min.

7.3 Calibration of GC

7.3.1 On a daily basis, inject 3 μ L of methyl tert-butyl ether directly into the GC to flush the system. Also purge the system with methyl tert-butyl ether injections between injections of standards and samples.

7.3.2 Inject 3 μ L of a sample blank (organic-free reagent water carried through the sample storage procedures and extracted with methyl tert-butyl ether).

7.3.3 Inject 3 μ L of at least five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte. The range of standard solution concentrations used should not exceed the working range of the GC system.

7.3.4 Prepare a calibration curve using the peak areas of the standards (retention time of acrylonitrile under the conditions of Section 7.2 is approximately 2.3 minutes). If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Section 7.4.2, for additional guidance on calibration by the external standard method.

7.4 Sample Analysis

7.4.1 Inject 3 μ L of the sample extract, using the same chromatographic conditions used to prepare the standard curve. Calculate

the concentration of acrylonitrile in the extract, using the area of the peak, against the calibration curve prepared in Section 7.3.4.

3.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

8.2 Prior to preparation of stock solutions, methanol and methyl tert-butyl ether reagents should be analyzed gas chromatographically under the conditions described in Section 7.2, to determine possible interferences with the acrylonitrile peak. If the solvent blanks show contamination, a different batch of solvents should be used.

9.0 METHOD PERFORMANCE

9.1 Method 8031 was tested in a single laboratory over a period of days. Duplicate samples and one spiked sample were run for each calculation. The GC was calibrated daily. Results are presented in Table 1.

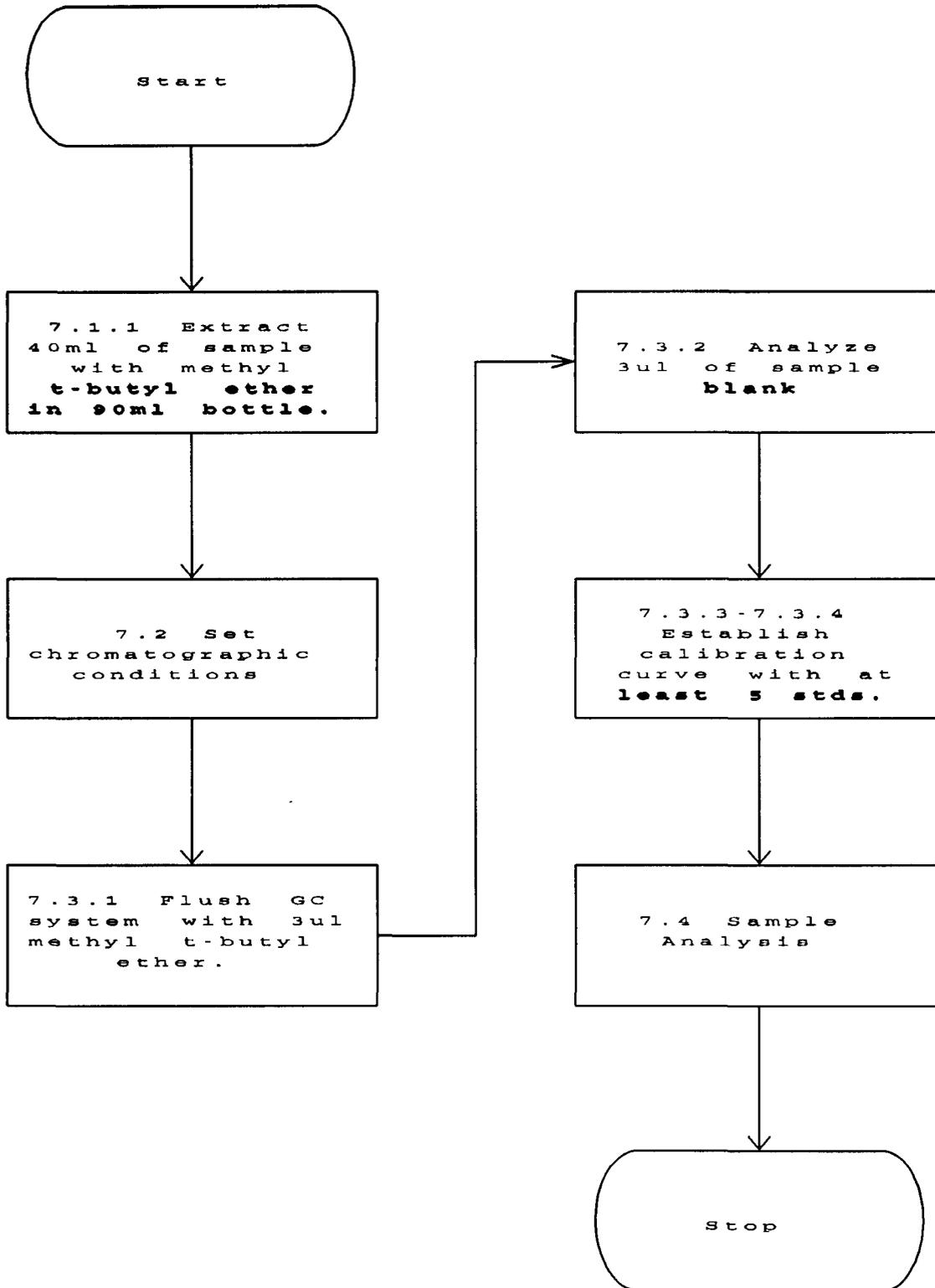
10.0 REFERENCES

1. K.L. Anderson, "The Determination of Trace Amounts of Acrylonitrile in Water by Specific Nitrogen Detector Gas Chromatograph", American Cyanamid Report No. WI-88-13, 1988.

TABLE 1
SINGLE LABORATORY METHOD PERFORMANCE

SAMPLE	CONCENTRATION SPIKE ($\mu\text{g/L}$)	% RECOVERY
A	60	100
B	60	105
C	40	86
D	40	100
E	40	88
F	60	94
Average		96

METHOD 8031
ACRYLONITRILE BY GAS CHROMATOGRAPHY



METHOD 8032

ACRYLAMIDE BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8032 is used to determine trace amounts of acrylamide monomer in aqueous matrices. This method may be applicable to other matrices. The following compounds can be determined by this method:

Compound Name	CAS No. ^a
Acrylamide	79-06-01

^a Chemical Abstract Services Registry Number.

1.2 The method detection limit (MDL) in clean water is 0.032 µg/L.

1.3 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Method 8032 is based on bromination of the acrylamide double bond. The reaction product (2,3-dibromopropionamide) is extracted from the reaction mixture with ethyl acetate, after salting out with sodium sulfate. The extract is cleaned up using a Florisil column, and analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 Compound identification should be supported by at least one additional qualitative technique. Analysis using a second gas chromatographic column or gas chromatography/mass spectrometry may be used for compound confirmation.

3.0 INTERFERENCES

3.1 No interference is observed from sea water or in the presence of 8.0% of ammonium ions derived from ammonium bromide. Impurities from potassium bromide are removed by the Florisil clean up procedure.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatographic System

4.1.1 Gas chromatograph suitable for on-column injections with all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Column: 2 m x 3 mm glass column, 5% FFAP (free fatty acid polyester) on 60-80 mesh acid washed Chromosorb W, or equivalent.

4.1.3 Detector: electron capture detector.

4.2 Kuderna-Danish (K-D) apparatus.

4.2.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Separatory funnel - 150 mL.

4.4 Volumetric flask (Class A) - 100 mL, with ground glass stopper; 25 mL, amber, with ground glass stopper.

4.5 Syringe - 5 mL.

4.6 Microsyringes - 5 μ L, 100 μ L.

4.7 Pipets (Class A).

4.8 Glass column (30 cm x 2 cm).

4.9 Mechanical shaker.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is

first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Ethyl acetate, $C_2H_5CO_2C_2H_5$. Pesticide quality, or equivalent.

5.3.2 Diethyl ether, $C_2H_5OC_2H_5$. Pesticide quality, or equivalent. Must be free of peroxides as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.3.3 Methanol, CH_3OH . Pesticide quality, or equivalent.

5.3.4 Benzene, C_6H_6 . Pesticide quality, or equivalent.

5.3.5 Acetone, CH_3COCH_3 . Pesticide quality, or equivalent.

5.4 Saturated bromine water. Prepare by shaking organic-free reagent water with bromine and allowing to stand for 1 hour, in the dark, at 4°C. Use the aqueous phase.

5.5 Sodium sulfate (anhydrous, granular), Na_2SO_4 . Purify by heating at 400°C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.6 Sodium thiosulfate, $Na_2S_2O_3$, 1 M aqueous solution.

5.7 Potassium bromide, KBr, prepared for infrared analysis.

5.8 Concentrated hydrobromic acid, HBr, specific gravity 1.48.

5.9 Acrylamide monomer, $H_2C:CHCONH_2$, electrophoresis reagent grade, minimum 95% purity.

5.10 Dimethyl phthalate, $C_6H_4(COOCH_3)_2$, 99.0% purity.

5.11 Florisil (60/100 mesh): Prepare Florisil by activating at 130°C for at least 16 hours. Alternatively, store Florisil in an oven at 130°C. Before use, cool the Florisil in a desiccator. Pack 5 g of the Florisil, suspended in benzene, in a glass column (Section 4.8).

5.12 Stock standard solutions

5.12.1 Prepare a stock standard solution of acrylamide monomer as specified in Section 5.12.1.1. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the

concentration of the stock standard. Commercially prepared standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.12.1.1 Dissolve 105.3 mg of acrylamide monomer in organic-free reagent water in a 100 mL volumetric flask, and dilute to the mark with organic-free reagent water. Dilute the solution of acrylamide monomer so as to obtain standard solutions containing 0.1 - 10 mg/L of acrylamide monomer.

5.13 Calibration standards

5.13.1 Dilute the acrylamide stock solution with organic-free reagent water to produce standard solutions containing 0.1 - 5 mg/L of acrylamide. Prior to injection the calibration standards are reacted and extracted in the same manner as environmental samples (Section 7).

5.14 Internal standards

5.14.1 The suggested internal standard is dimethyl phthalate. Prepare a solution containing 100 mg/L of dimethyl phthalate in ethyl acetate. The concentration of dimethyl phthalate in the sample extracts and calibration standards should be 4 mg/L.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Bromination

7.1.1 Pipet 50 mL of sample into a 100 mL glass stoppered flask. Dissolve 7.5 g of potassium bromide into the sample, with stirring.

7.1.2 Adjust the pH of the solution with concentrated hydrobromic acid until the pH is between 1 and 3.

7.1.3 Wrap the flask with aluminum foil in order to exclude light. Add 2.5 mL of saturated bromine water, with stirring. Store the flask and contents in the dark, at 0°C, for at least 1 hour.

7.1.4 After reacting the solution for at least an hour, decompose the excess of bromine by adding 1 M sodium thiosulfate solution, dropwise, until the color of the solution is discharged.

7.1.5 Add 15 g of sodium sulfate, using a magnetic stirrer to effect vigorous stirring.

7.2 Extraction

7.2.1 Transfer the solution into a 150 mL separatory funnel. Rinse the reaction flask three times with 1 mL aliquots of organic-free reagent water. Transfer the rinsings into the separatory funnel.

7.2.2 Extract the aqueous solution with two 10 mL portions of ethyl acetate for 2 min each, using a mechanical shaker (240 strokes per min). Dry the organic phase with 1 g of sodium sulfate.

7.2.3 Transfer the organic phase into a 25 mL amber volumetric flask. Rinse the sodium sulfate with three 1.5 mL portions of ethyl acetate and combine the rinsings with the organic phase.

7.2.4 Add exactly 100 μ g of dimethyl phthalate to the flask and make the solution up to the 25 mL mark with ethyl acetate. Inject 5 μ L portions of this solution into the gas chromatograph.

7.3 Florisil cleanup: Whenever interferences are observed, the samples should be cleaned up as follows.

7.3.1 Transfer the dried extract into a Kuderna-Danish evaporator with 15 mL of benzene. Evaporate the solvent at 70°C under reduced pressure, and concentrate the solution to about 3 mL.

7.3.2 Add 50 mL of benzene and subject the solution to Florisil column chromatography at a flow rate of 3 mL/min. Elute the column first with 50 mL of diethyl ether/benzene (1:4) at a flow rate of 5 mL/min, and then with 25 mL of acetone/benzene (2:1) at a flow rate of 2 mL/min. Discard all of the first eluate and the initial 9 mL portion of the second eluate, and use the remainder for the determination, using dimethyl phthalate (4 mg/L) as an internal standard.

NOTE: Benzene is toxic, and should be only be used under a ventilated laboratory hood.

7.4 Gas chromatographic conditions:

Nitrogen carrier gas flow rate:	40 mL/min
Column temperature:	165°C.
Injector temperature:	180°C
Detector temperature:	185°C.
Injection volume:	5 μ L

7.5 Calibration:

7.5.1 Inject 5 μ L of a sample blank (organic-free reagent water carried through all sample storage, handling, bromination and extraction procedures).

7.5.2 Prepare standard solutions of acrylamide as described in Section 5.13.1. Brominate and extract each standard solution as described in Sections 7.1 and 7.2.

7.5.2.1 Inject 5 μL of each of a minimum of five standard solutions: one should be near the detection limit; one should be near, but below, the expected concentrations of the analyte; one should be near, but above, the expected concentrations of the analyte.

7.5.2.2 Prepare a calibration curve using the peak areas of the standards. If the calibration curve deviates significantly from a straight line, prepare a new calibration curve with the existing standards, or, prepare new standards and a new calibration curve. See Method 8000, Section 7.4.3, for additional guidance on calibration by the internal standard method.

7.5.2.3 Calculate the response factor for each standard according to Equation 1.

$$\text{RF} = \frac{(P_s) (M_{is})}{(P_{is}) (M_A)} \quad \text{Equation 1}$$

RF = Response factor
 P_s = Peak height of acrylamide
 M_{is} = Amount of internal standard injected (ng)
 P_{is} = Peak height of internal standard
 M_A = Amount of acrylamide injected (ng)

7.5.3 Calculate the mean response factor according to Equation 2.

$$\overline{\text{RF}} = \frac{\sum_{i=1}^n \text{RF}}{n} \quad \text{Equation 2}$$

$\overline{\text{RF}}$ = Mean response factor
 RF = Response factors from standard analyses (calculated in Equation 1)
 n = Number of analyses

7.6 Gas chromatographic analysis:

7.6.1 Inject 5 μL portions of each sample (containing 4 mg/L internal standard) into the gas chromatograph. An example GC/ECD chromatogram is shown in Figure 1.

7.6.2 The concentration of acrylamide monomer in the sample is given by Equation 3.

$$[A] = \frac{(P_A) (M_{is})}{(P_{is}) (\overline{\text{RF}}) (V_i) (V_s)} \quad \text{Equation 3}$$

[A] = Concentration of acrylamide monomer in sample (mg/L)
 P_A = Peak height of acrylamide monomer

M_{is}	=	Amount of internal standard injected (ng)
V_s	=	Total volume of sample (mL)
P_{is}	=	Peak height of internal standard
\overline{RF}	=	Mean response factor from Equation 2
V_i	=	Injection volume (μ L)

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control procedures.

9.0 METHOD PERFORMANCE

9.1 The following performance data have been generated under the conditions described in this method:

9.1.1 The calibration curve for Method 8032 is linear over the range 0-5 μ g/L of acrylamide monomer.

9.1.2 The limit of detection for an aqueous solution is 0.032 μ g/L.

9.1.3 The yields of the brominated compound are $85.2 \pm 3.3\%$ and $83.3 \pm 0.9\%$, at fortification concentrations of 1.0 and 5.0 μ g/L, respectively.

9.2 Table 1 provides the recoveries of acrylamide monomer from river water, sewage effluent, and sea water.

9.3 The recovery of the bromination product as a function of the amount of potassium bromide and hydrobromic acid added to the sample is shown in Figure 2.

9.4 The effect of the reaction time on the recovery of the bromination product is shown in Figure 3. The yield was constant when the reaction time was more than 1 hour.

9.5 Figure 4 shows the recovery of the bromination product as a function of the initial pH from 1 to 7.35. The yield was constant within this pH range. The use of conventional buffer solutions, such as sodium acetate - acetic acid solution or phosphate solution, caused a significant decrease in yield.

10.0 REFERENCES

1. Hashimoto, A., "Improved Method for the Determination of Acrylamide Monomer in Water by Means of Gas-Liquid Chromatography with an Electron-capture Detector," Analyst, 101:932-938, 1976.

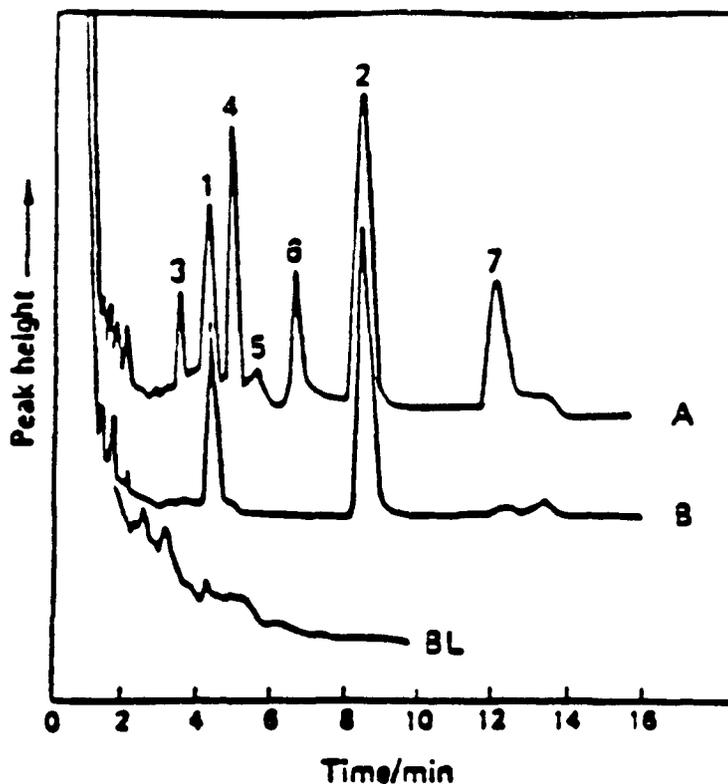
TABLE 1
RECOVERY OF ACRYLAMIDE FROM WATER SAMPLES AS
2,3-DIBROMOPROPIONAMIDE

Sample Matrix	Acrylamide Monomer Spiked/ μg	Amount of 2,3-DBPA ^a / μg		Overall Bromination Recovery % ^b	Recovery of Acrylamide Monomer, % ^b	Coefficient of Variation
		Calculated	Found ^b			
Standard	0.05	0.162	0.138	85.2	---	3.3
	0.20	0.649	0.535	82.4	---	1.0
	0.25	0.812	0.677	83.3	---	0.9
River Water	0.20	0.649	0.531	81.8	99.4	2.5
Sewage Effluent	0.20	0.649	0.542	83.5	101.3	3.0
Sea Water	0.20	0.649	0.524	80.7	98.8	3.5

^a 2,3-Dibromopropionamide

^b Mean of five replicate determinations

Figure 1



Typical gas chromatograms of the bromination product obtained from aqueous acrylamide monomer solution:

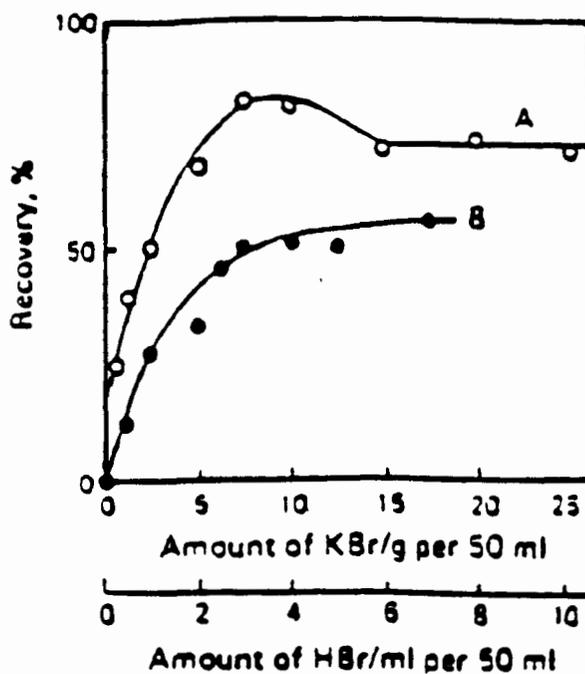
- A. Untreated
- B. With Florisil cleanup
- BL. Chromatogram of blank, concentrated five-fold before gas chromatographic analysis.

Peaks:

- 1. 2,3-Dibromopropionamide
- 2. Dimethyl phthalate
- 4-7. Impurities from potassium bromide

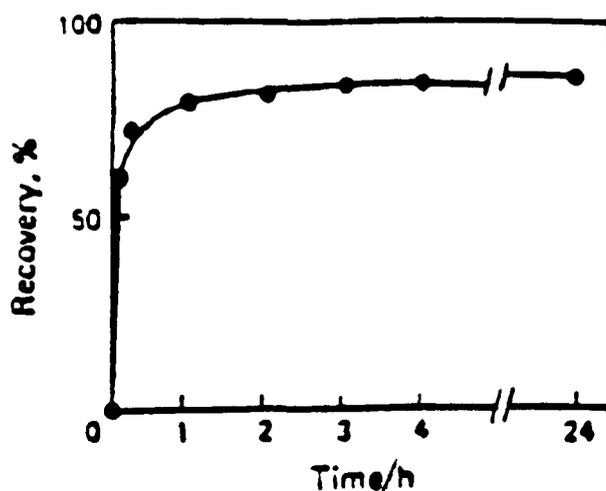
Sample size = 100 mL; acrylamide monomer = 0.1 μ g

Figure 2



Effect of (A) potassium bromide and (B) hydrobromic acid on the yield of bromination. Sample size = 50 mL; acrylamide monomer = 0.25 μ g

Figure 3



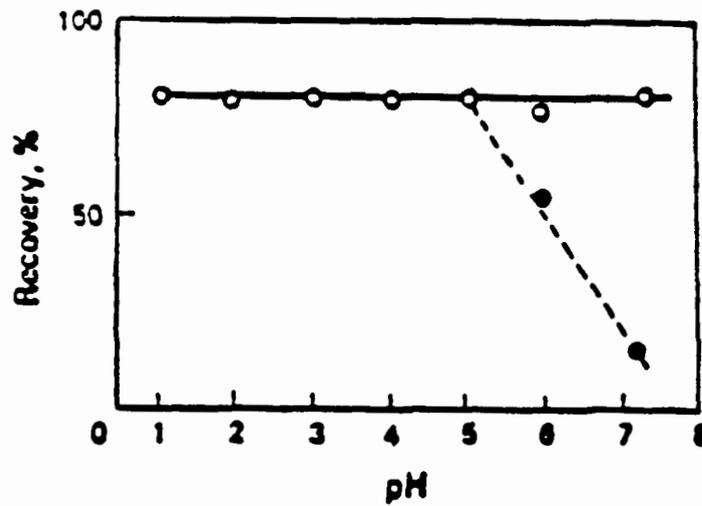
Effect of reaction time on the bromination. Reaction conditions:

50 mL of sample;
0.25 μ g of acrylamide monomer;
7.5 g of potassium bromide;
2.5 mL of saturated bromine water

Extraction conditions:

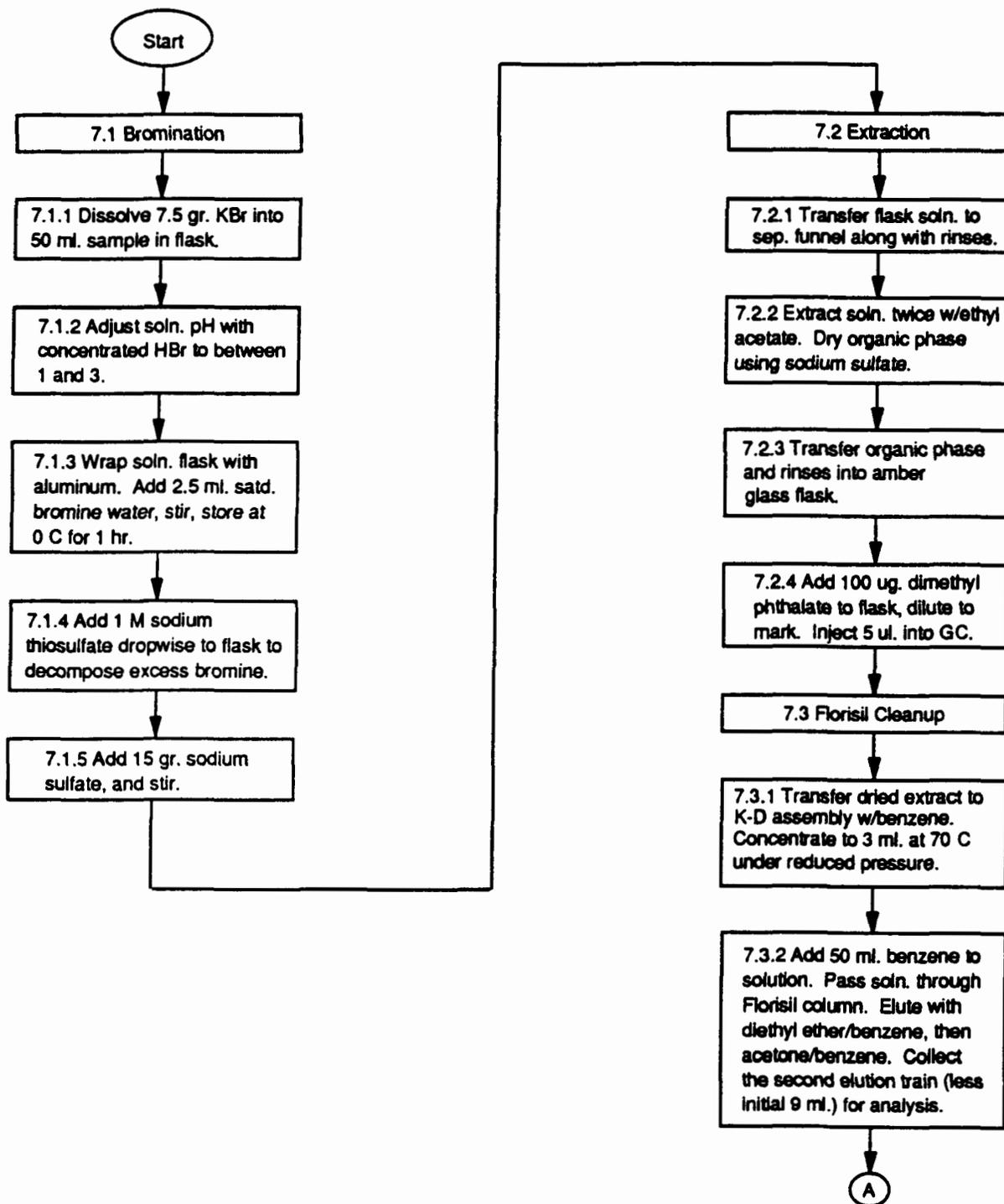
15 g of sodium sulfate;
extraction at pH 2;
solvent = 10 mL of ethyl acetate (X2)

Figure 4

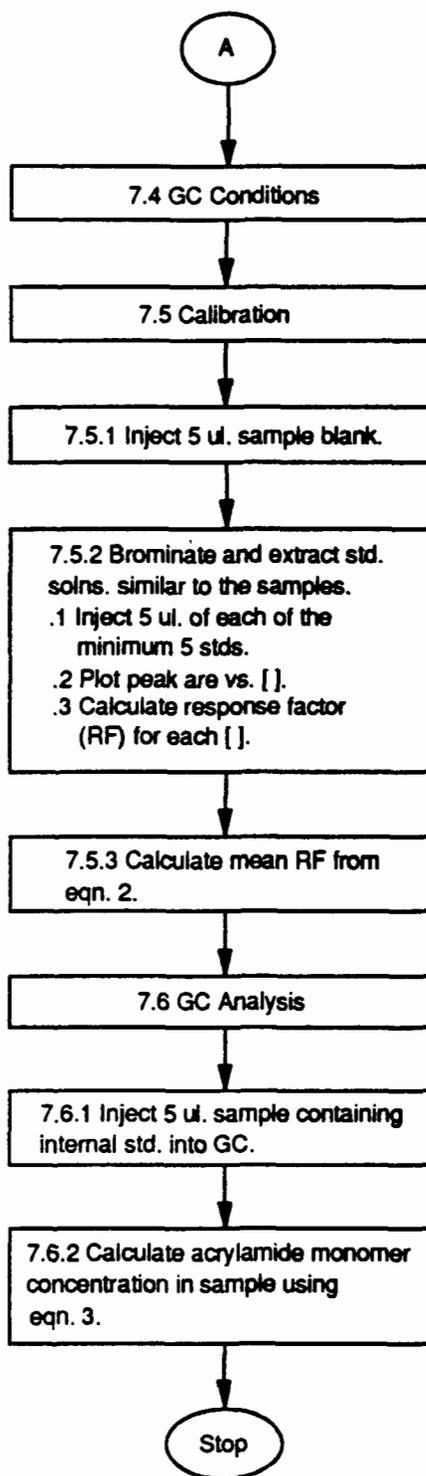


Effect of initial pH on the bromination. Reaction and extraction conditions as in Figure 3. The pH was adjusted to below 3 with concentrated hydrobromic acid, and to 4-5 with dilute hydrobromic acid. Reaction at pH 6 was in distilled water. pH 7.35 was achieved by careful addition of dilute sodium hydroxide solution. The broken line shows the result obtained by the use of sodium acetate - acetic acid buffer solution.

METHOD 8032
ACRYLAMIDE BY GAS CHROMATOGRAPHY



METHOD 8032
continued



METHOD 8040

PHENOLS

1.0 SCOPE AND APPLICATION

1.1 Method 8040 is used to determine the concentration of various phenolic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in water. Table 2 lists the practical quantitation limit (PQL) for all matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8040 provides gas chromatographic conditions for the detection of phenolic compounds. Prior to analysis, samples must be extracted using appropriate techniques (see Chapter Two for guidance). Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph using the solvent flush technique, and compounds in the GC effluent are detected by a flame ionization detector (FID).

2.2 Method 8040 also provides for the preparation of pentafluorobenzyl-bromide (PFB) derivatives, with additional cleanup procedures for electron capture gas chromatography. This is to reduce detection limits of some phenols and to aid the analyst in the elimination of interferences.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

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

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

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph - Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.2 Columns

4.1.2.1 Column for underivatized phenols - 1.8 m x 2.0 mm i.d. glass column packed with 1% SP-1240DA on Supelcoport 80/100 mesh or equivalent.

4.1.2.2 Column for derivatized phenols - 1.8 m x 2 mm i.d. glass column packed with 5% OV-17 on Chromosorb W-AW-DMCS 80/100 mesh or equivalent.

4.1.3 Detectors - Flame ionization (FID) and electron capture (ECD).

4.2 Reaction vial - 20-mL, with Teflon lined cap.

4.3 Volumetric flask - 10-, 50-, and 100-mL, ground-glass stopper.

4.4 Kuderna-Danish (K-D) apparatus

4.4.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.4.2 Evaporation flask - 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

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).

4.5 Boiling chips - Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath - Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.7 Microsyringe - 10-uL.

4.8 Syringe - 5-mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Hexane, $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$. Pesticide quality or equivalent.

5.4 2-Propanol, $(\text{CH}_3)_2\text{CHOH}$. Pesticide quality or equivalent.

5.5 Toluene, $\text{C}_6\text{H}_5\text{CH}_3$. Pesticide quality or equivalent.

5.6 Derivatization reagent - Add 1 mL pentafluorobenzyl bromide and 1 g 18-crown-6-ether to a 50-mL volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly. This operation should be carried out in a hood. Store at 4°C and protect from light.

5.6.1 Pentafluorobenzyl bromide (alpha-Bromopentafluorotoluene), $\text{C}_6\text{F}_5\text{CH}_2\text{Br}$. 97% minimum purity.

NOTE: This chemical is a lachrymator.

5.6.2 18-crown-6-ether (1,4,7,10,13,16-Hexaoxacyclooctadecane) - 98% minimum purity.

NOTE: This chemical is highly toxic.

5.7 Potassium carbonate (Powdered), K_2CO_3 .

5.8 Stock standard solutions

5.8.1 Prepare stock standard solution at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in 2-propanol and diluting to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.8.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.8.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.9 Calibration standards - Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with 2-propanol. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC.

Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.10 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.10.1 Prepare calibration standards at a minimum of five concentrations for each analyte as described in Step 5.9.

5.10.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with 2-propanol.

5.10.3 Analyze each calibration standard according to Section 7.0.

5.11 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and water blank with phenolic surrogates (e.g. 2-fluorophenol and 2,4,6-tribromophenol) recommended to encompass the range of the temperature program used in this method. Method 3500, Step 5.3.1.1, details instructions on the preparation of acid surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of less than or equal to 2 with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. Extracts obtained from application of either Method 3540 or 3550 should undergo Acid-Base Partition Cleanup, using Method 3650.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to 2-propanol. The exchange is performed during the micro K-D procedures listed in all of the extraction methods. The exchange is performed as follows:

7.1.2.1 Following concentration of the extract to 1 mL using the macro- Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 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. Add one or two clean boiling chips to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of 2-propanol to the top. Place the 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 liquid reaches 2.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Add an additional 2 mL of 2-propanol, add one or two clean boiling chips to the concentrator tube, and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.3 Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw-cap. If the extract requires no further derivatization or cleanup, proceed with gas chromatographic analysis.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Column for underivatized phenols - Set nitrogen gas flow at 30 mL/min flow rate. Set column temperature at 80°C and immediately program an 8°C/min temperature rise to 150°C; hold until all compounds have eluted.

7.2.2 Column for derivatized phenols - Set 5% methane/95% argon gas flow at 30 mL/min flow rate. Set column temperature at 200°C isothermal.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used for the underivatized phenols. Refer to Method 8000 for a description of each of these procedures. If derivatization of the phenols is required, the method of external calibration should be used by injecting five or more levels of calibration standards that have also undergone derivatization and cleanup prior to instrument calibration.

7.4 Gas chromatographic analysis

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Phenols are to be determined on a gas chromatograph equipped with a flame ionization detector according to the conditions listed for the 1% SP-1240DA column (Step 7.2.1). Table 1 summarizes estimated retention times and sensitivities that should be achieved by this method for clean water samples. Practical quantitation limits for other matrices are list in Table 2.

7.4.3 Follow Step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

7.4.4 An example of a GC/FID chromatogram for certain phenols is shown in Figure 1. Other packed or capillary (open-tubular) columns, chromatographic conditions, or detectors may be used if the requirements of Step 8.2 are met.

7.4.5 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.6 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. See Step 7.8 of Method 8000 for calculation equations.

7.4.7 If peak detection using the SP-1240DA column with the flame ionization detector is prevented by interferences, PFB derivatives of the phenols should be analyzed on a gas chromatograph equipped with an electron capture detector according to the conditions listed for the 5% OV-17 column (Step 7.2.2). The derivatization and cleanup procedure is outlined in Steps 7.5 through 7.6. Table 3 summarizes estimated retention times for derivatives of some phenols using the conditions of this method.

7.4.8 Figure 2 shows a GC/ECD chromatogram of PFB derivatives of certain phenols.

7.4.9 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.10 Determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes. The method of external calibration should be used (see Method 8000 for guidance). The concentration of the individual compounds in the sample is calculated as follows:

$$\text{Concentration (ug/L)} = [(A)(V_t)(B)(D)] / [(V_i)(X)(C)(E)]$$

where:

A = Mass of underivatized phenol represented by area of peak in sample chromatogram, determined from calibration curve (see Method 8000 Step 7.4.2), ng.

V_t = Total amount of column eluate or combined fractions from which V_i was taken, μL .

B = Total volume of hexane added in Step 7.5.5, mL.

D = Total volume of 2-propanol extract prior to derivatization, mL.

V_i = Volume injected, μL .

X = Volume of water extracted, mL, or weight of nonaqueous sample extracted, g, from Step 7.1. Either the dry or wet weight of the nonaqueous sample may be used, depending upon the specific application of the data.

C = Volume of hexane sample solution added to cleanup column (Method 3630, Step 7.2), mL.

E = Volume of 2-propanol extract carried through derivatization in Step 7.5.1, mL.

7.5 Derivatization - If interferences prevent measurement of peak area during analysis of the extract by flame ionization gas chromatography, the phenols must be derivatized and analyzed by electron capture gas chromatography.

7.5.1 Pipet a 1.0-mL aliquot of the 2-propanol stock standard solution or of the sample extract into a glass reaction vial. Add 1.0 mL derivatization reagent (Step 5.3). This amount of reagent is sufficient to derivatize a solution whose total phenolic content does not exceed 0.3 mg/mL.

7.5.2 Add approximately 3 mg of potassium carbonate to the solution and shake gently.

7.5.3 Cap the mixture and heat it for 4 hours at 80°C in a hot water bath.

7.5.4 Remove the solution from the hot water bath and allow it to cool.

7.5.5 Add 10 mL hexane to the reaction vial and shake vigorously for 1 minute. Add 3.0 mL water to the reaction vial and shake for 2 minutes.

7.5.6 Decant the organic layer into a concentrator tube and cap with a glass stopper. Proceed with cleanup procedure.

7.6 Cleanup

7.6.1 Cleanup of the derivatized extracts takes place using Method 3630 (Silica Gel Cleanup), in which specific instructions for cleanup of the derivatized phenols appear.

7.6.2 Following column cleanup, analyze the samples using GC/ECD, as described starting in Step 7.4.7.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method used. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Step 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Step 8.6) should contain each analyte of interest at a concentration of 100 ug/mL in 2-propanol.

8.2.2 Table 4 indicates the calibration and QC acceptance criteria for this method. Table 5 gives method accuracy and precision as functions of concentration for the analytes. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 12 to 450 ug/L. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the analyte and essentially independent of the sample

matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 5.

9.2 The accuracy and precision obtained will be affected by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

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TABLE 1.
FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compound	Retention time (minutes)	Method Detection limit (ug/L)
2-sec-Butyl-4,6-dinitrophenol (DNBP)		
4-Chloro-3-methylphenol	7.50	0.36
2-Chlorophenol	1.70	0.31
Cresols (methyl phenols)		
2-Cyclohexyl-4,6-dinitrophenol		
2,4-Dichlorophenol	4.30	0.39
2,6-Dichlorophenol		
2,4-Dimethylphenol	4.03	0.32
2,4-Dinitrophenol	10.00	13.0
2-Methyl-4,6-dinitrophenol	10.24	16.0
2-Nitrophenol	2.00	0.45
4-Nitrophenol	24.25	2.8
Pentachlorophenol	12.42	7.4
Phenol	3.01	0.14
Tetrachlorophenols		
Trichlorophenols		
2,4,6-Trichlorophenol	6.05	0.64

TABLE 2.
DETERMINATION OF PRACTICAL QUANTITATION
LIMITS (PQL) FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

^aSample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

^bPQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
ELECTRON CAPTURE GAS CHROMATOGRAPHY OF PFB DERIVATIVES

Parent compound	Retention time (min)	Method detection limit (ug/L)
4-Chloro-2-methylphenol	4.8	1.8
2-Chlorophenol	3.3	0.58
2,4-Dichlorophenol	5.8	0.68
2,4-Dimethylphenol	2.9	0.63
2,4-Dinitrophenol	46.9	
2-Methyl-4,6-dinitrophenol	36.6	
2-Nitrophenol	9.1	0.77
4-Nitrophenol	14.0	0.70
Pentachlorophenol	28.8	0.59
Phenol	1.8	2.2
2,4,6-Trichlorophenol	7.0	0.58

TABLE 4.
QC ACCEPTANCE CRITERIA^a

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for \bar{x} (ug/L)	Range P, P _s (%)
4-Chloro-3-methylphenol	100	16.6	56.7-113.4	99-122
2-Chlorophenol	100	27.0	54.1-110.2	38-126
2,4-Dichlorophenol	100	25.1	59.7-103.3	44-119
2,4-Dimethylphenol	100	33.3	50.4-100.0	24-118
4,6-Dinitro-2-methylphenol	100	25.0	42.4-123.6	30-136
2,4-Dinitrophenol	100	36.0	31.7-125.1	12-145
2-Nitrophenol	100	22.5	56.6-103.8	43-117
4-Nitrophenol	100	19.0	22.7-100.0	13-110
Pentachlorophenol	100	32.4	56.7-113.5	36-134
Phenol	100	14.1	32.4-100.0	23-108
2,4,6-Trichlorophenol	100	16.6	60.8-110.4	53-119

s = Standard deviation of four recovery measurements, in ug/L.

\bar{x} = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

^aCriteria from 40 CFR Part 136 for Method 604. These criteria are based directly upon the method performance data in Table 5. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 5.

TABLE 5.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION^a

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
4-Chloro-3-methylphenol	0.87C-1.97	0.11 \bar{x} -0.21	0.16 \bar{x} +1.41
2-Chlorophenol	0.83C-0.84	0.18 \bar{x} +0.20	0.21 \bar{x} +0.75
2,4-Dichlorophenol	0.81C+0.48	0.17 \bar{x} -0.02	0.18 \bar{x} +0.62
2,4-Dimethylphenol	0.62C-1.64	0.30 \bar{x} -0.89	0.25 \bar{x} +0.48
4,6-Dinitro-2-methylphenol	0.84C-1.01	0.15 \bar{x} +1.25	0.19 \bar{x} +5.85
2,4-Dinitrophenol	0.80C-1.58	0.27 \bar{x} -1.15	0.29 \bar{x} +4.51
2-Nitrophenol	0.81C-0.76	0.15 \bar{x} +0.44	0.14 \bar{x} +3.84
4-Nitrophenol	0.46C+0.18	0.17 \bar{x} +2.43	0.19 \bar{x} +4.79
Pentachlorophenol	0.83C+2.07	0.22 \bar{x} -0.58	0.23 \bar{x} +0.57
Phenol	0.43C+0.11	0.20 \bar{x} -0.88	0.17 \bar{x} +0.77
2,4,6-Trichlorophenol	0.86C-0.40	0.10 \bar{x} +0.53	0.13 \bar{x} +2.40

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of \bar{x} , in ug/L.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{x} , in ug/L.

C = True value for the concentration, in ug/L.

\bar{x} = Average recovery found for measurements of samples containing a concentration of C, in ug/L.

^aFrom 40 CFR Part 136 for Method 604.

Figure 1.
Gas chromatogram of phenols.

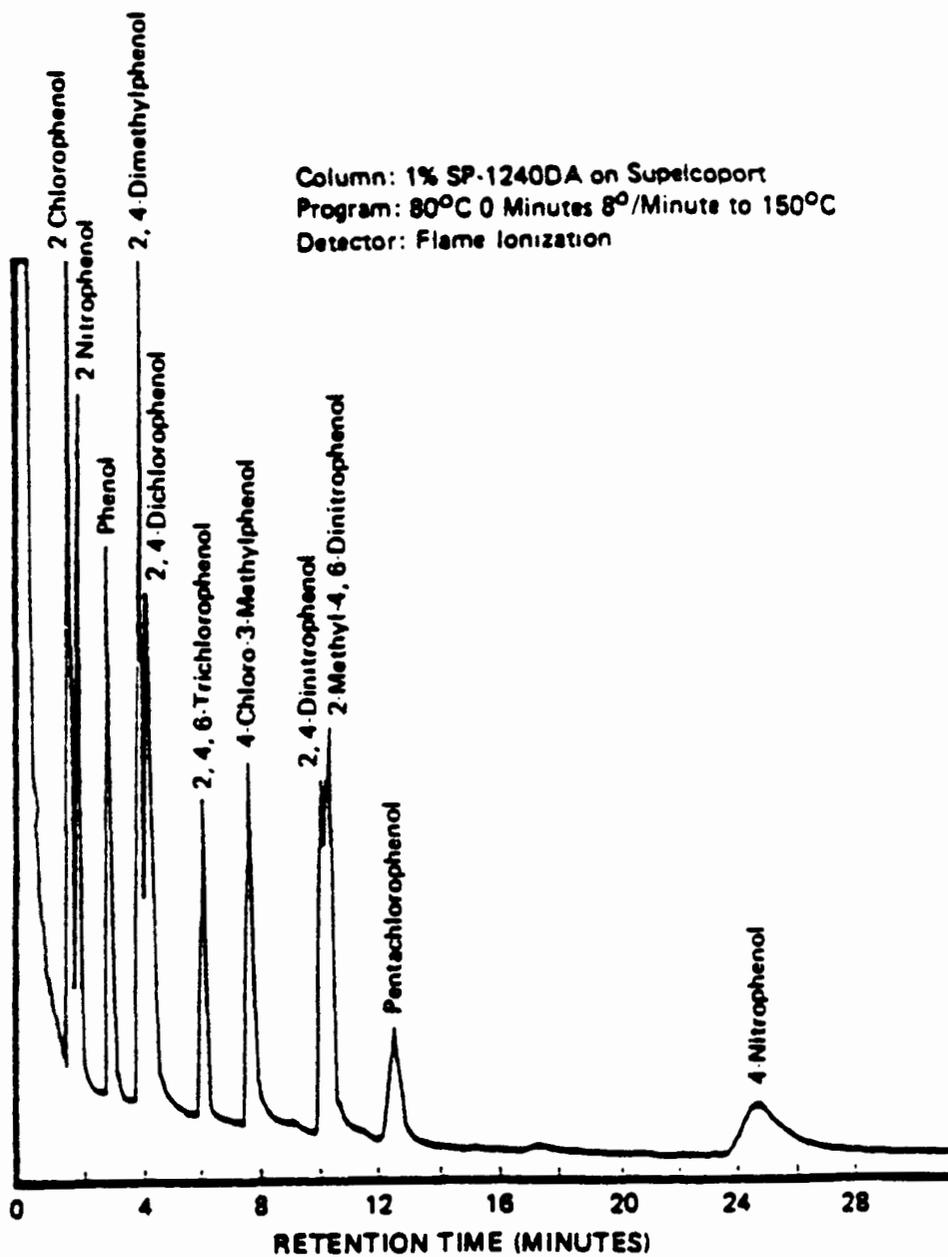
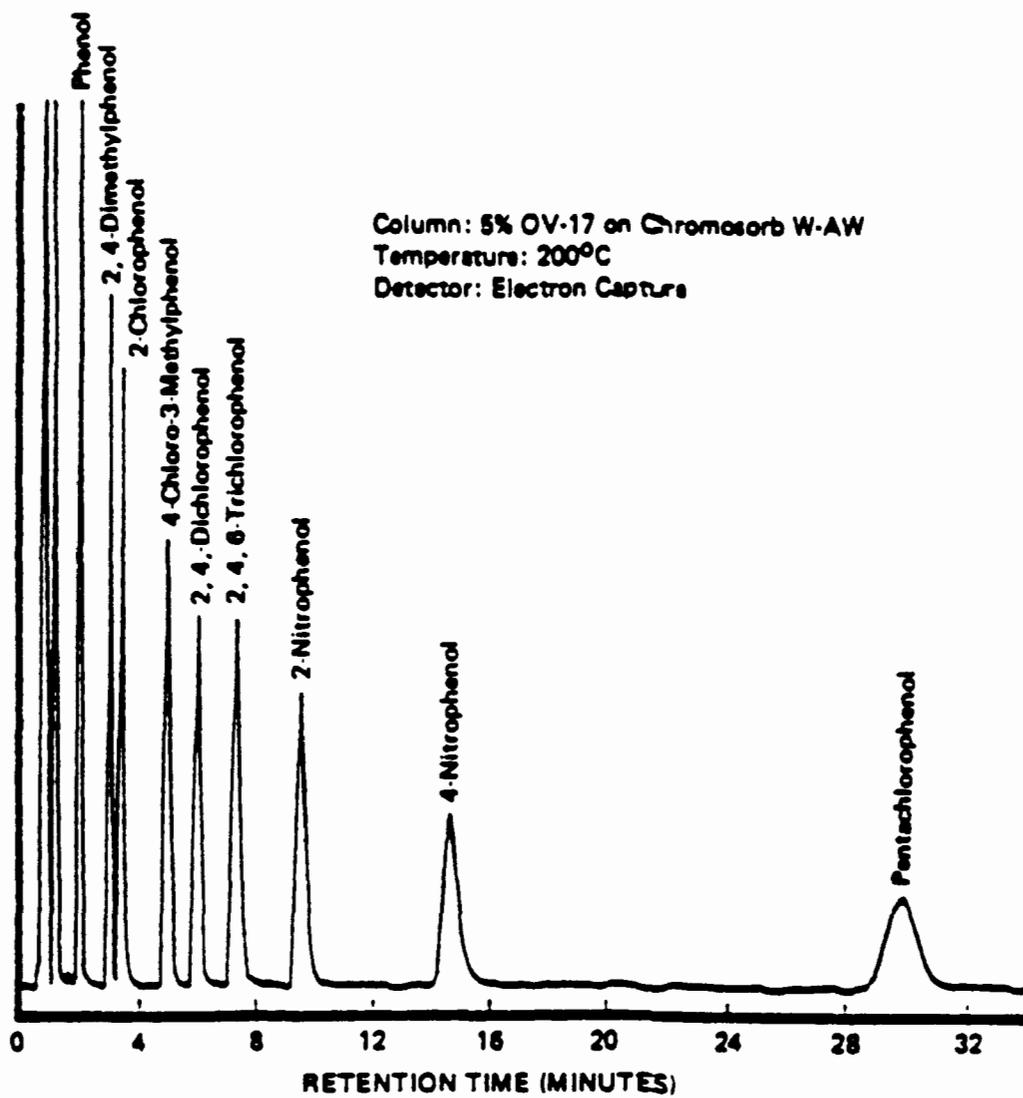
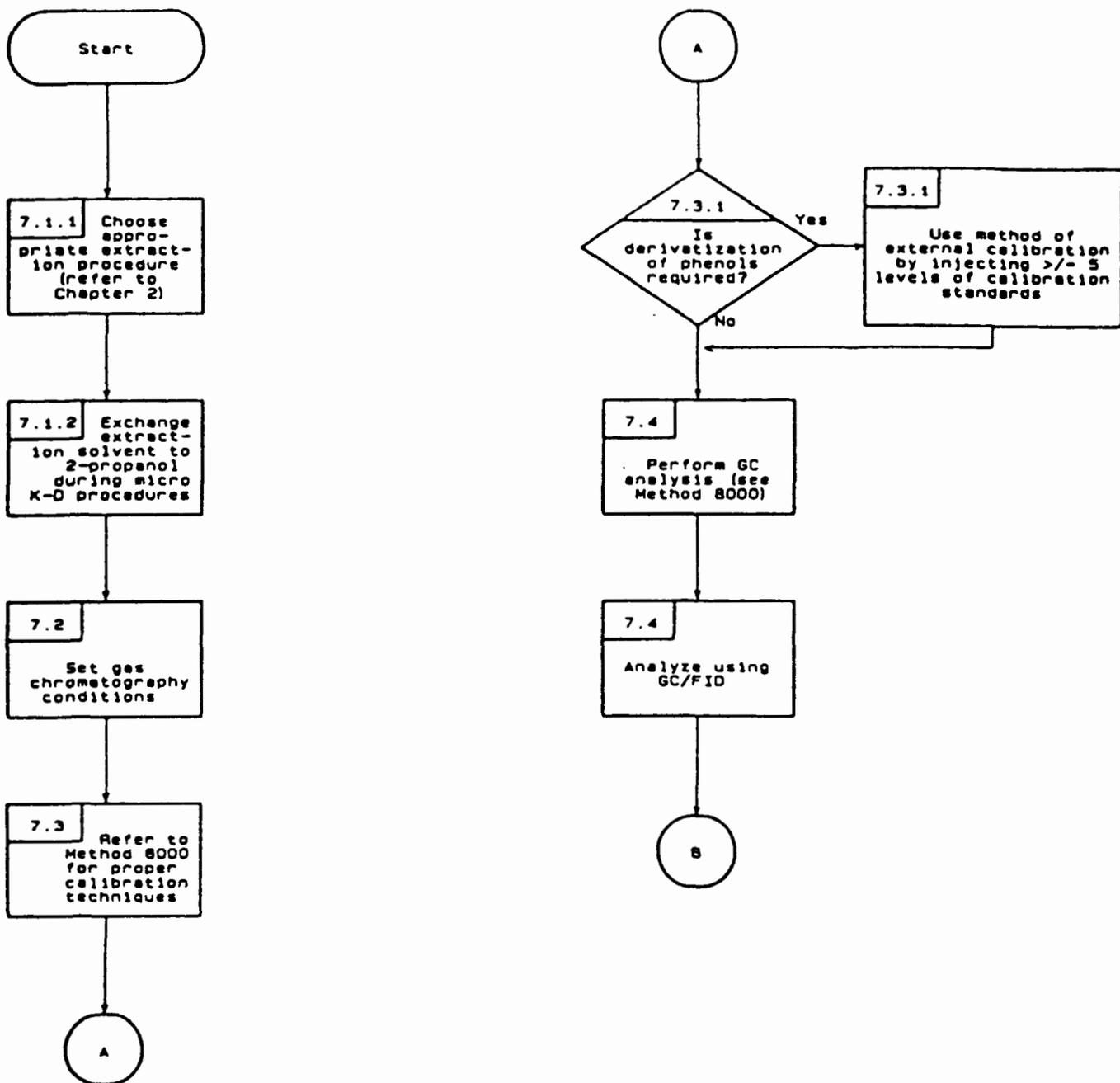


Figure 2.

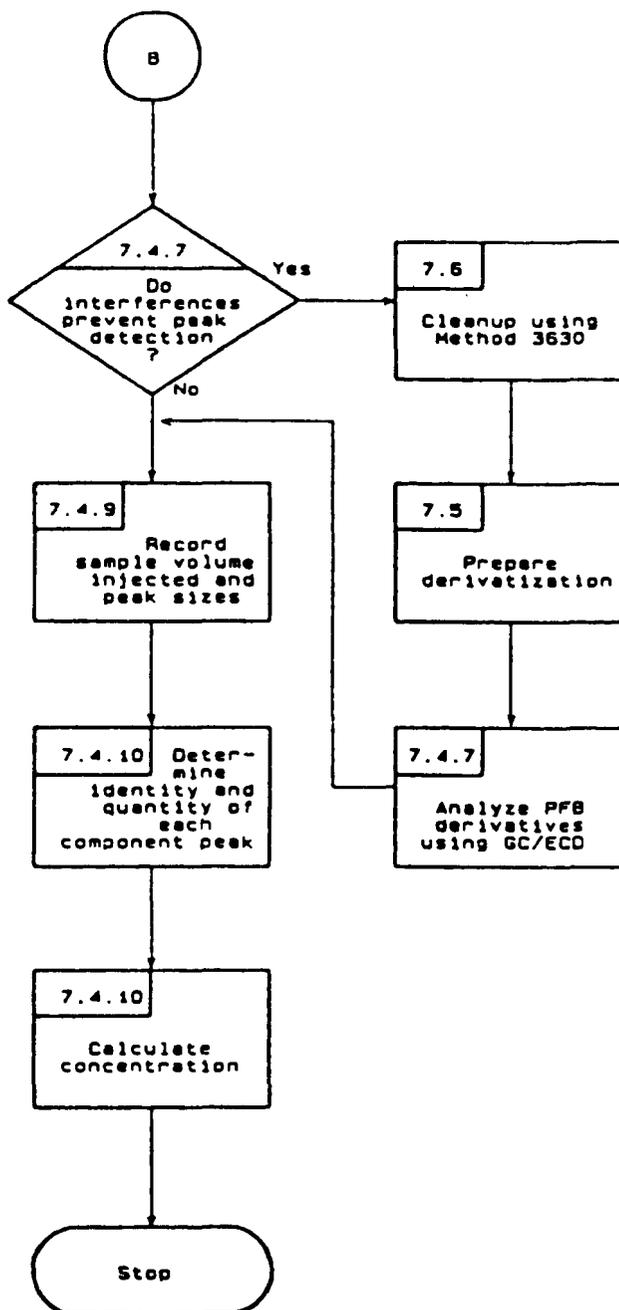
Gas chromatogram of PFB derivatives of phenols.



METHOD 8040
PHENOLS



METHOD 8040
(Continued)



METHOD 8061

PHTHALATE ESTERS BY CAPILLARY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTION (GC/ECD)

1.0 SCOPE AND APPLICATION

1.1 Method 8061 is used to determine the identities and concentrations of various phthalate esters in liquid, solid and sludge matrices. The following compounds can be determined by this method:

<u>Compound Name</u>	<u>CAS No.</u> ^a
Benzyl benzoate (I.S.)	120-51-4
Bis(2-ethylhexyl) phthalate	117-81-7
Butyl benzyl phthalate	85-68-7
Di-n-butyl phthalate	84-74-2
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
Di-n-octyl phthalate	117-84-0

^a Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limits (MDL) for the target analytes in a water matrix. The MDLs for the components of a specific sample may differ from those listed in Table 1 because MDLs depend on the nature of interferences in the sample matrix. Table 2 lists the estimated quantitation limits (EQL) for other matrices.

1.3 When this method is used to analyze for any or all of the target analytes, compound identification should be supported by at least one additional qualitative technique. This method describes conditions for parallel column, dual electron capture detector analysis which fulfills the above requirement. Retention time information obtained on two megabore fused-silica open tubular columns is given in Table 1. Alternatively, gas chromatography/mass spectrometry could be used for compound confirmation.

1.4 The following compounds, bis(2-n-butoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, bis(2-methoxyethyl) phthalate, bis(4-methyl-2-pentyl) phthalate, diamyl phthalate, dicyclohexyl phthalate, dihexyl phthalate, diisobutyl phthalate, dinonyl phthalate, and hexyl 2-ethylhexyl phthalate can also be analyzed by this method and may be used as surrogates.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample (approximately 1 liter for liquids, 10 to 30 grams for solids and sludges) is extracted by using the appropriate sample extraction technique specified in Methods 3510, 3540, and 3550. Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate, bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Aqueous samples are extracted at a pH of 5 to 7, with methylene chloride, in a separatory funnel (Method 3510). Alternatively, particulate-free aqueous samples could be filtered through membrane disks that contain C₁₈-bonded silica. The phthalate esters are retained by the silica and, later eluted with acetonitrile. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with an ultrasonic extractor (Method 3550). After cleanup, the extract is analyzed by gas chromatography with electron capture detection (GC/ECD).

2.2 The sensitivity of Method 8061 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, cleanup of the sample extracts is necessary. Either Method 3610 or 3620 alone or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis. Method 3640, Gel Permeation Cleanup, is applicable for samples that contain high amounts of lipids and waxes.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences coextracted from the samples will vary considerably from waste to waste. While general cleanup techniques are referenced or provided as part of this method, unique samples may require additional cleanup approaches to achieve desired sensitivities for the target analytes.

3.3 Glassware must be scrupulously clean. All glassware require treatment in a muffle furnace at 400 °C for 2 to 4 hrs, or thorough rinsing with pesticide-grade solvent, prior to use. Refer to Chapter 4, Section 4.1.4, for further details regarding the cleaning of glassware. Volumetric glassware should not be heated in a muffle furnace.

If Soxhlet extractors are baked in the muffle furnace, care must be taken to ensure that they are dry (breakage may result if any water is left in the side-arm). Thorough rinsing with hot tap water, followed by deionized water and acetone is not an adequate decontamination procedure. Even after a Soxhlet extractor was refluxed with acetone for three days, with daily solvent changes, the concentrations of bis(2-ethylhexyl) phthalate were as high as 500 ng per washing. Storage of glassware in the laboratory introduces contamination, even if the glassware is wrapped in aluminum foil. Therefore, any glassware used in Method 8061 should be cleaned immediately prior to use.

3.4 Florisil and alumina may be contaminated with phthalate esters and, therefore, use of these materials in sample cleanup should be employed cautiously. If these materials are used, they must be obtained packaged in glass

(plastic packaging will contribute to contamination with phthalate esters). Washing of these materials prior to use with the solvent(s) used for elution during extract cleanup was found helpful, however, heating at 320 °C for Florisil and 210 °C for alumina is recommended. Phthalate esters were detected in Florisil cartridge method blanks at concentrations ranging from 10 to 460 ng, with 5 phthalate esters in the 105 to 460 ng range. Complete removal of the phthalate esters from Florisil cartridges does not seem possible, and it is therefore desirable to keep the steps involved in sample preparation to a minimum.

3.5 Paper thimbles and filter paper must be exhaustively washed with the solvent that will be used in the sample extraction. Soxhlet extraction of paper thimbles and filter paper for 12 hrs with fresh solvent should be repeated for a minimum of three times. Method blanks should be obtained before any of the precleaned thimbles or filter papers are used. Storage of precleaned thimbles and filter paper in precleaned glass jars covered with aluminum foil is recommended.

3.6 Glass wool used in any step of sample preparation should be a specially treated pyrex wool, pesticide grade, and must be baked at 400°C for 4 hrs. immediately prior to use.

3.7 Sodium sulfate must be obtained packaged in glass (plastic packaging will contribute to contamination with phthalate esters), and must be purified by heating at 400 °C for 4 hrs. in a shallow tray, or by precleaning with methylene chloride (Section 5.3). To avoid recontamination, the precleaned material must be stored in glass-stoppered glass bottles, or glass bottles covered with precleaned aluminum foil. The storage period should not exceed two weeks. To minimize contamination, extracts should be dried directly in the glassware in which they are collected by adding small amounts of precleaned sodium sulfate until an excess of free flowing material is noted.

3.8 The presence of elemental sulfur will result in large peaks which often mask the region of the compounds eluting before dicyclohexyl phthalate (Compound No. 14) in the gas chromatograms shown in Figure 1. Method 3660 is suggested for removal of sulfur.

3.9 Waxes and lipids can be removed by Gel Permeation Chromatography (Method 3640). Extracts containing high concentrations of lipids are viscous, and may even solidify at room temperature.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatography

4.1.1 Gas chromatograph, analytical system complete with gas chromatograph suitable for on-column and split/splitless injections and all required accessories, including detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.1.1 Eight inch injection tee (Supelco, Inc., Catalog No. 2-3665, or equivalent) or glass Y splitter for megabore columns (J&W Scientific, "press-fit", Catalog No. 705-0733, or equivalent).

4.1.2 Columns

4.1.2.1 Column 1, 30 m x 0.53 mm ID, 5% phenyl/95% methyl silicone fused-silica open tubular column (DB-5, J&W Scientific, or equivalent), 1.5 μm film thickness.

4.1.2.2 Column 2, 30 m x 0.53 mm ID, 14% cyanopropyl phenyl silicone fused-silica open tubular column (DB-1701, J&W Scientific, or equivalent), 1.0 μm film thickness.

4.1.3 Detector - Dual electron capture detector (ECD)

4.2 Glassware, see Methods 3510, 3540, 3550, 3610, 3620, 3640, and 3660 for specifications.

4.3 Kuderna-Danish (K-D) apparatus.

4.3.1 Concentrator tube - 10 mL graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

4.3.2 Evaporation flask - 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.3.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.3.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.3.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.4 Boiling chips, approximately 10/40 mesh. Heat to 400 °C for 30 min, or Soxhlet-extract with methylene chloride prior to use.

4.5 Water bath, heated, with concentric ring cover, capable of temperature control ($\pm 2^\circ\text{C}$).

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Sodium sulfate (granular, anhydrous), Na_2SO_4 . Purify by heating at 400 °C for 4 hours in a shallow tray, or by precleaning the sodium sulfate with methylene chloride. If the sodium sulfate is precleaned with methylene chloride, a method blank must be analyzed, demonstrating that there is no interference from the sodium sulfate.

5.4 Solvents:

5.4.1 Hexane, C_6H_{14} - Pesticide quality, or equivalent.

5.4.2 Methylene chloride, CH_2Cl_2 - Pesticide quality, or equivalent.

5.4.3 Acetone, CH_3COCH_3 - Pesticide quality, or equivalent.

5.4.4 Acetonitrile, CH_3CN - HPLC grade.

5.4.5 Methanol, CH_3OH - HPLC grade.

5.4.6 Diethyl Ether, $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ - Pesticide quality, or equivalent. Must be free of peroxides, as indicated by test strips (EM Quant, or equivalent). Procedures for removal of peroxides are provided with the test strips. After cleanup, 20 mL of ethyl alcohol preservative must be added to each liter of ether.

5.5 Stock standard solutions:

5.5.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in hexane, and diluting to volume in a 10 mL volumetric flask. When compound purity is assayed to be 96 percent or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standard solutions can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.2 Transfer the stock standard solutions into glass vials with Teflon lined screw-caps or crimp tops. Store at 4 °C and protect from light. Stock standard solutions should be checked periodically by gas chromatography for signs of degradation or evaporation, especially just prior to preparation of calibration standards.

5.5.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.6 Calibration standards: Calibration standards are prepared at a minimum of five concentrations for each parameter of interest through dilution of the stock standard solutions with hexane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples, or should define the working range of the GC. Calibration solutions must be replaced after 1 to 2 months, or sooner if comparison with calibration verification standards indicates a problem.

5.7 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Benzyl benzoate has been tested and found appropriate for Method 8061.

5.7.1 Prepare a spiking solution of benzyl benzoate in hexane at 5000 mg/L. Addition of 10 μ L of this solution to 1 mL of sample extract is recommended. The spiking concentration of the internal standard should be kept constant for all samples and calibration standards. Store the internal standard spiking solution at 4 °C in glass vials with Teflon lined screw-caps or crimp tops. Standard solutions should be replaced when ongoing QC (Section 8) indicates a problem.

5.8 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), analytical system, and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and blank with surrogate compounds. Three surrogates may be used for Method 8061 in addition to those listed in Section 1.4: diphenyl phthalate, diphenyl isophthalate, and dibenzyl phthalate. However, the compounds listed in Section 1.4 are recommended.

5.8.1 Prepare a surrogate standard spiking solution, in acetone, which contains 50 ng/ μ L of each compound. Addition of 500 μ L of this solution to 1 L of water or 30 g solid sample is equivalent to 25 μ g/L of water or 830 μ g/kg of solid sample. The spiking concentration of the surrogate standards may be adjusted accordingly, if the final volume of extract is reduced below 2 mL for water samples or 10 mL for solid samples. Store the surrogate spiking solution at 4 °C in glass vials with Teflon lined screw-caps or crimp tops. The solution must be replaced after 6 months, or sooner if ongoing QC (Section 8) indicates problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a pH of 5 to 7 with methylene chloride in a separatory funnel (Method 3510). Method 3520 is not recommended for the extraction of aqueous samples because the longer chain esters (dihexyl phthalate bis(2-ethylhexyl) phthalate, di-n-octyl phthalate, and dinonyl phthalate) tend to adsorb to the glassware and consequently, their extraction recoveries are <40 percent. Solid samples are extracted with hexane/acetone (1:1) or methylene chloride/acetone (1:1) in a Soxhlet extractor (Method 3540) or with an ultrasonic extractor (Method 3550). Immediately prior to

extraction, spike 500 μL of the surrogate standard spiking solution (concentration = 50 ng/ μL) into 1 L aqueous sample or 30 g solid sample.

7.1.2 Extraction of particulate-free aqueous samples using C_{18} -extraction disks (optional):

7.1.2.1 Disk preconditioning: Place the C_{18} -extraction disk into the filtration apparatus and prewash the disk with 10 to 20 mL of acetonitrile. Apply vacuum to pull the solvent through the disk. Maintain vacuum to pull air through for 5 min. Follow with 10 mL of methanol. Apply vacuum and pull most of the methanol through the disk. Release vacuum before the disk gets dry. Follow with 10 mL organic-free reagent water. Apply vacuum and pull most of the water through the disk. Release the vacuum before the disk gets dry.

7.1.2.2 Sample preconcentration: Add 2.5 mL of methanol to the 500 mL aqueous sample in order to get reproducible results. Pour the sample into the filtration apparatus. Adjust vacuum so that it takes approximately 20 min to process the entire sample. After all of the sample has passed through the membrane disk, pull air through the disk for 5 to 10 min. to remove any residual water.

7.1.2.3 Sample elution: Break the vacuum and place the tip of the filter base into the test tube that is contained inside the suction flask. Add 10 mL of acetonitrile to the graduated funnel, making sure to rinse the walls of the graduated funnel with the solvent. Apply vacuum to pass the acetonitrile through the membrane disk.

7.1.2.4 Extract concentration (if necessary): Concentrate the extract to 2 mL or less, using either the micro Snyder column technique (Section 7.1.2.4.1) or nitrogen blowdown technique (Section 7.1.2.4.2).

7.1.2.4.1 Micro Snyder Column Technique

7.1.2.4.1.1 Add one or two clean boiling chips to the concentrator tube and attach a two ball micro Snyder column. Prewet the column by adding about 0.5 mL of acetonitrile to the top of the column. Place the K-D apparatus in a hot water bath (15-20 $^{\circ}\text{C}$ above the boiling point of the solvent) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 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 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints with

about 0.2 mL of solvent and add to the concentrator tube. Adjust the final volume to 1.0-2.0 mL with solvent.

7.1.2.4.2 Nitrogen Blowdown Technique

7.1.2.4.2.1 Place the concentrator tube in a warm water bath (approximately 35 °C) and evaporate the solvent volume to the required level using a gentle stream of clean, dry nitrogen (filtered through a column of activated carbon).

CAUTION: Do not use plasticized tubing between the carbon trap and the sample.

7.1.2.4.2.2 The internal wall of the tube must be rinsed down several times with acetonitrile during the operation. During evaporation, the solvent level in the tube must be positioned to prevent water from condensing into the sample (i.e., the solvent level should be below the level of the water bath). Under normal operating conditions, the extract should not be allowed to become dry.

7.2 Solvent Exchange: Prior to Florisil cleanup or gas chromatographic analysis, the methylene chloride and methylene chloride/acetone extracts obtained in Section 7.1.1 must be exchanged to hexane, as described in Sections 7.2.1 through 7.2.3. Exchange is not required for the acetonitrile extracts obtained in Section 7.1.2.4.

7.2.1 Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Concentrate the extract as described in Section 7.1.2.4.1, using 1 mL of methylene chloride to prewet the column, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes.

7.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and attach the macro Snyder column. Concentrate the extract as described in Section 7.1.2.4.1, using 1 mL of hexane to prewet the Snyder column, raising the temperature of the water bath, if necessary, to maintain proper distillation, and completing the concentration in 10-20 minutes. When the apparent volume of liquid reaches 1-2 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL hexane. A 5 mL syringe is recommended for this operation. Adjust the extract volume to 2 mL for water samples, using either the micro Snyder column technique (Section 7.1.2.4.1) or nitrogen blowdown technique (Section 7.1.2.4.2), or 10 mL for solid samples. Stopper the concentrator tube and store at 4 °C if further processing will be performed immediately. If the extract will be

stored for two days or longer, it should be transferred to a glass vial with a Teflon lined screw-cap or crimp top. Proceed with the gas chromatographic analysis.

7.3 Cleanup/Fractionation:

7.3.1 Cleanup may not be necessary for extracts from a relatively clean sample matrix. If polychlorinated biphenyls (PCBs) and organochlorine pesticides are known to be present in the sample, use the procedure outlined in Methods 3610 or 3620. When using column cleanup, collect Fraction 1 by eluting with 140 mL (Method 3610) or 100 mL (Method 3620) of 20-percent diethyl ether in hexane. Note that, under these conditions, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are not recovered from the Florisil column. The elution patterns and compound recoveries are given in Table 3.

7.3.2 Methods 3610 and 3620 also describe procedures for sample cleanup using Alumina and Florisil Cartridges. With this method, bis(2-methoxyethyl) phthalate, bis(2-ethoxyethyl) phthalate, and bis(2-n-butoxyethyl) phthalate are recovered quantitatively.

7.4 Gas chromatographic conditions (recommended):

7.4.1 Column 1 and Column 2 (Section 4.1.2):

Carrier gas (He) =	6 mL/min.
Injector temperature =	250 °C.
Detector temperature =	320 °C.
Column temperature:	
Initial temperature =	150 °C, hold for 0.5 min.
Temperature program =	150 °C to 220 °C at 5 °C/min., followed by 220 °C to 275 °C at 3 °C/min.
Final temperature =	275 °C hold for 13 min.

7.4.2 Table 1 gives the retention times and MDLs that can be achieved by this method for the 16 phthalate esters. An example of the separations achieved with the DB-5 and DB-1701 fused-silica open tubular columns is shown in Figure 1.

7.5 Calibration:

7.5.1 Refer to Method 8000 for proper calibration techniques. Use Tables 1 and 2 for guidance on selecting the lowest point on the calibration curve.

7.5.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for the description of each of these procedures.

7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 μL of internal standard solution at 5000 mg/L to the sample prior to injection.

7.6.2 Follow Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria.

7.6.3 Record the sample volume injected and the resulting peak areas.

7.6.4 Using either the internal or the external calibration procedure (Method 8000), determine the identity and the quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.6.5 If the response of a peak exceeds the working range of the system, dilute the extract and reanalyze.

7.6.6 Identify compounds in the sample by comparing the retention times of the peaks in the sample chromatogram with those of the peaks in standard chromatograms. The retention time window used to make identifications is based upon measurements of actual retention time variations over the course of 10 consecutive injections. Three times the standard deviation of the retention time can be used to calculate a suggested window size.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC specified in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain the test compounds at 5 to 10 ng/ μL .

8.3 Calculate the recoveries of the surrogate compounds for all samples, method blanks, and method spikes. Determine if the recoveries are within limits established by performing QC procedures outlined in Method 8000.

8.3.1 If the recoveries are not within limits, the following are required:

8.3.1.1 Make sure there are no errors in calculations, surrogate solutions and internal standards. Also check instrument performance.

8.3.1.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.3.1.3 Reextract and reanalyze the sample if none of the above are a problem, or flag the data as "estimated concentration."

8.4 An internal standard peak area check must be performed on all samples. The internal standard must be evaluated for acceptance by determining whether the measured area for the internal standard deviates by more than 30 percent from the average area for the internal standard in the calibration standards. When the internal standard peak area is outside that limit, all samples that fall outside the QC criteria must be reanalyzed.

8.5 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory-generated detection limits.

8.5.1 The GC/MS would normally require a minimum concentration of 10 ng/ μ L in the final extract for each single-component compound.

8.5.2 The sample extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270. Normally, analysis of a blank is not required for confirmation analysis, however, analysis for phthalates is a special case because of the possibility for sample contamination through septum punctures, etc.

8.5.3 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a concentration that would demonstrate the ability to confirm the phthalate esters identified by GC/ECD.

8.6 Include a mid-concentration calibration standard after each group of 20 samples in the analysis sequence. The response factors for the mid-concentration calibration must be within \pm 15 percent of the average values for the multiconcentration calibration.

8.7 Demonstrate through the analyses of standards that the Florisil fractionation scheme is reproducible. When using the fractionation schemes given in Methods 3610 or 3620, batch-to-batch variations in the composition of the alumina or Florisil material may cause variations in the recoveries of the phthalate esters.

9.0 METHOD PERFORMANCE

9.1 The MDL is defined in Chapter One. The MDL concentrations listed in Table 1 were obtained using organic-free reagent water. Details on how to determine MDLs are given in Chapter One. The MDL actually achieved in a given analysis will vary, as it is dependent on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory by using different types of aqueous samples and solid samples which were fortified with the test compounds at two concentrations. Single-operator precision, overall precision,

and method accuracy were found to be related to the concentration of the compounds and the type of matrix. Results of the single-laboratory method evaluation are presented in Tables 6 and 7.

9.3 The accuracy and precision obtained is determined by the sample matrix, sample preparation technique, cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. Glazer, J.A.; Foerst, G.D.; McKee, G.D.; Quave, S.A., and Budde, W.L., "Trace Analyses for Wastewaters," Environ. Sci. and Technol. 15: 1426, 1981.
2. Lopez-Avila, V., Baldin, E., Benedicto, J., Milanes, J., and Beckert, W.F., "Application of Open-Tubular Columns to SW-846 GC Methods", EMSL-Las Vegas, 1990.
3. Beckert, W.F. and Lopez-Avila, V., "Evaluation of SW-846 Method 8060 for Phthalate Esters", Proceedings of Fifth Annual Testing and Quality Assurance Symposium, USEPA, 1989.

TABLE 1.
GAS CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS FOR THE PHTHALATE ESTERS^a

Compound No.	Compound name	Chemical Abstract Registry No.	Retention time ^a (min)		MDL ^b
			Column 1	Column 2	Liquid (ng/L)
1	Dimethyl phthalate	131-11-3	7.06	6.37	640
2	Diethyl phthalate	84-66-2	9.30	8.45	250
3	Diisobutyl phthalate	84-69-5	14.44	12.91	120
4	Di-n-butyl phthalate	84-74-2	16.26	14.66	330
5	Bis(4-methyl-2-pentyl) phthalate	146-50-9	18.77	16.27	370
6	Bis(2-methoxyethyl) phthalate	117-82-8	17.02	16.41	510
7	Diamyl phthalate	131-18-0	20.25	18.08	110
8	Bis(2-ethoxyethyl) phthalate	605-54-9	19.43	18.21	270
9	Hexyl 2-ethylhexyl phthalate	75673-16-4	21.07	18.97	130
10	Dihexyl phthalate	84-75-3	24.57	21.85	68
11	Butyl benzyl phthalate	85-68-7	24.86	23.08	42
12	Bis(2-n-butoxyethyl) phthalate	117-83-9	27.56	25.24	84
13	Bis(2-ethylhexyl) phthalate	117-81-7	29.23	25.67	270
14	Dicyclohexyl phthalate	84-61-7	28.88	26.35	22
15	Di-n-octyl phthalate	117-84-0	33.33	29.83	49
16	Dinonyl phthalate	84-76-4	38.80	33.84	22
IS	Benzyl benzoate	120-51-4	12.71	11.07	^c
SU-1	Diphenyl phthalate	84-62-8	29.46	28.32	^c
SU-2	Diphenyl isophthalate	744-45-6	32.99	31.37	^c
SU-3	Dibenzyl phthalate	523-31-9	34.40	32.65	^c

Table 1. (continued)

- ^a Column 1 is a 30 m x 0.53 mm ID DB-5 fused-silica open tubular column (1.5 μm film thickness). Column 2 is a 30 m 0.53 mm ID DB-1701 fused-silica open tubular column (1.0 μm film thickness). Temperature program is 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min. An 8-in Supelco injection tee or a J&W Scientific press fit glass inlet splitter is used to connect the two columns to the injection port of a gas chromatograph. Carrier gas helium at 6 mL/min; makeup gas nitrogen at 20 mL/min; injector temperature 250°C; detector temperature 320°C.
- ^b MDL is the method detection limit. The MDL was determined from the analysis of seven replicate aliquots of organic-free reagent water processed through the entire analytical method (extraction, Florisil cartridge cleanup, and GC/ECD analysis using the single column approach: DB-5 fused-silica capillary column). $\text{MDL} = t_{(n-1, 0.99)} \times \text{SD}$ where $t_{(n-1, 0.99)}$ is the student's t value appropriate for a 99 percent confidence interval and a standard deviation with $n-1$ degrees of freedom, and SD is the standard deviation of the seven replicate measurements. Values measured were not corrected for method blanks.
- ^c Not applicable.

TABLE 2.
ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Groundwater	10
Low-concentration soil by ultrasonic extraction with GPC cleanup	670
High-concentration soil and sludges by ultrasonic extraction	10,000
Non-water miscible waste	100,000

^a Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

^b EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For nonaqueous samples, the factor is on a wet weight basis.

TABLE 3.
AVERAGE RECOVERIES OF METHOD 8061 COMPOUNDS USING METHODS 3610 AND 3620

Compound	Alumina column ^a	Florisil column ^a	Alumina cartridge ^b	Florisil cartridge ^d
Dimethyl phthalate	64.5	40.0	101	89.4
Diethyl phthalate	62.5	57.0	103	97.3
Diisobutyl phthalate	77.0	80.0	104	91.8
Di-n-butyl phthalate	76.5	85.0	108	102
Bis(4-methyl-2-pentyl) phthalate	89.5	84.5	103	105
Bis(2-methoxyethyl) phthalate	70.5	0	64.1 ^c	78.3 ^e
Diamyl phthalate	75.0	81.5	103	94.5
Bis(2-ethoxyethyl) phthalate	67.0	0	111	93.6
Hexyl 2-ethylhexyl phthalate	90.5	105	101	96.0
Dihexyl phthalate	73.0	74.5	108	96.8
Benzyl butyl phthalate	87.0	90.0	103	98.6
Bis(2-n-butoxyethyl) phthalate	62.5	0	108	91.5
Bis(2-ethylhexyl) phthalate	91.0	82.0	97.6	97.5
Dicyclohexyl phthalate	84.5	83.5	97.5	90.5
Di-n-octyl phthalate	108	115	112	97.1
Dinonyl phthalate	71.0	72.5	97.3	105

^a 2 determinations; alumina and Florisil chromatography performed according to Methods 3610 and 3620, respectively.

^b 2 determinations, using 1 g alumina cartridges; Fraction 1 was eluted with 5 mL of 20-percent acetone in hexane. 40 µg of each component was spiked per cartridge.

^c 36.8 percent was recovered by elution with an additional 5 mL of 20-percent acetone in hexane.

^d 2 determinations, using 1 g Florisil cartridges; Fraction 1 was eluted with 5 mL of 10-percent acetone in hexane. 40 µg of each component was spiked per cartridge.

^e 14.4 percent was recovered by elution with an additional 5 mL of 10-percent acetone in hexane.

TABLE 6.
ACCURACY AND PRECISION DATA FOR METHOD 3510 AND METHOD 8061^a

Estuarine Compound	Spike Concentration (20 µg/L)			Spike Concentration (60 µg/L)		
	water	Leachate	Estuarine Groundwater	water	Leachate	Groundwater
Dimethyl phthalate	84.0 (4.1)	98.9 (19.6)	87.1 (8.1)	87.1 (7.5)	112 (17.5)	90.9 (4.5)
Diethyl phthalate	71.2 (3.8)	82.8 (19.3)	88.5 (15.3)	71.0 (7.7)	88.5 (17.9)	75.3 (3.5)
Diisobutyl phthalate	76.0 (6.5)	95.3 (16.9)	92.7 (17.1)	99.1 (19.0)	100 (9.6)	83.2 (3.3)
Di-n-butyl phthalate	83.2 (6.5)	97.5 (22.3)	91.0 (10.7)	87.0 (8.0)	106 (17.4)	87.7 (2.7)
Bis(4-methyl-2-pentyl) phthalate	78.6 (2.6)	87.3 (18.2)	92.6 (13.7)	97.4 (15.0)	107 (13.3)	87.6 (2.9)
Bis(2-methoxyethyl) phthalate	73.8 (1.0)	87.2 (21.7)	82.4 (4.4)	82.5 (5.5)	99.0 (13.7)	76.9 (6.6)
Diamyl phthalate	78.2 (7.3)	92.1 (21.5)	88.8 (7.5)	89.2 (2.8)	112 (14.2)	92.5 (1.8)
Bis(2-ethoxyethyl) phthalate	75.6 (3.3)	90.8 (22.4)	86.4 (5.8)	88.7 (4.9)	109 (14.6)	84.8 (5.9)
Hexyl 2-ethylhexyl phthalate	84.7 (5.3)	91.1 (27.5)	81.4 (17.6)	107 (16.8)	117 (11.4)	80.1 (4.1)
Dihexyl phthalate	79.8 (7.2)	102 (21.5)	90.9 (7.6)	90.1 (2.4)	109 (20.7)	88.9 (2.4)
Benzyl butyl phthalate	84.1 (6.4)	105 (20.5)	89.6 (6.1)	92.7 (5.6)	117 (24.7)	93.0 (2.0)
Bis(2-n-butoxyethyl) phthalate	78.5 (3.5)	92.3 (16.1)	89.3 (3.6)	86.1 (6.2)	107 (15.3)	92.4 (0.6)
Bis(2-ethylhexyl) phthalate	81.4 (4.1)	93.0 (15.0)	90.5 (4.9)	86.5 (6.9)	108 (15.1)	91.1 (3.0)
Dicyclohexyl phthalate	77.4 (6.5)	88.2 (13.2)	91.7 (15.2)	87.7 (9.6)	102 (14.3)	71.9 (2.4)
Di-n-octyl phthalate	74.9 (4.9)	87.5 (18.7)	87.2 (3.7)	85.1 (8.3)	105 (17.7)	90.4 (2.0)
Dinonyl phthalate	59.5 (6.1)	77.3 (4.2)	67.2 (8.0)	97.2 (7.0)	108 (17.9)	90.1 (1.1)
Surrogates:						
Diphenyl phthalate	98.5 (2.6)	113 (14.9)	110 (3.3)	110 (12.4)	95.1 (7.2)	107 (2.4)
Diphenyl isophthalate	95.8 (1.9)	112 (11.7)	109 (3.3)	104 (5.9)	97.1 (7.1)	106 (2.8)
Dibenzyl phthalate	93.9 (4.4)	112 (14.0)	106 (3.8)	111 (5.9)	93.3 (9.5)	105 (2.4)

^a The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries.

TABLE 7.
ACCURACY AND PRECISION DATA FOR METHOD 3550 AND METHOD 8061^a

Compound	Spike Concentration (1 mg/kg)			Spike Concentration (3 µg/g)		
	Estuarine sediment	Municipal sludge	Sandy loam soil	Estuarine sediment	Municipal sludge	Sandy loam soil
Dimethyl phthalate	77.9 (42.8)	52.1 (35.5)	^c	136 (9.6)	64.8 (11.5)	70.2 (2.0)
Diethyl phthalate	68.4 (1.7)	68.6 (9.1)	54.7 (6.2)	60.2 (12.5)	72.8 (10.0)	67.0 (15.1)
Diisobutyl phthalate	103 (3.1)	106 (5.3)	70.3 (3.7)	74.8 (6.0)	84.0 (4.6)	79.2 (0.1)
Di-n-butyl phthalate	121 (25.8)	86.3 (17.7)	72.6 (3.7)	74.6 (3.9)	113 (5.8)	70.9 (5.5)
Bis(4-methyl-2-pentyl) phthalate	108 (57.4)	97.3 (7.4)	^c	104 (1.5)	150 (6.1)	83.9 (11.8)
Bis(2-methoxyethyl) phthalate	26.6 (26.8)	72.7 (8.3)	0	19.5 (14.8)	59.9 (5.4)	0
Diamyl phthalate	95.0 (10.2)	81.9 (7.1)	81.9 (15.9)	77.3 (4.0)	116 (3.7)	82.1 (15.5)
Bis(2-ethoxyethyl) phthalate	^c	66.6 (4.9)	^c	21.7 (22.8)	57.5 (9.2)	84.7 (8.5)
Hexyl 2-ethylhexyl phthalate	^c	114 (10.5)	57.7 (2.8)	72.7 (11.3)	26.6 (47.6)	28.4 (4.3)
Dihexyl phthalate	103 (3.6)	96.4 (10.7)	77.9 (2.4)	75.5 (6.8)	80.3 (4.7)	79.5 (2.7)
Benzyl butyl phthalate	113 (12.8)	82.8 (7.8)	56.5 (5.1)	72.9 (3.4)	76.8 (10.3)	67.3 (3.8)
Bis(2-n-butoxyethyl) phthalate	114 (21.1)	74.0 (15.6)	^c	38.3 (25.1)	98.0 (6.4)	62.0 (3.4)
Bis(2-ethylhexyl) phthalate	^c	76.6 (10.6)	99.2 (25.3)	59.5 (18.3)	85.8 (6.4)	65.4 (2.8)
Dicyclohexyl phthalate	36.6 (48.8)	65.8 (15.7)	92.8 (35.9)	33.9 (66.1)	68.5 (9.6)	62.2 (19.1)
Di-n-octyl phthalate	^c	93.3 (14.6)	84.7 (9.3)	36.8 (16.4)	88.4 (7.4)	115 (29.2)
Dinonyl phthalate	^c	80.0 (41.1)	64.2 (17.2)	^c	156 (8.6)	115 (13.2)

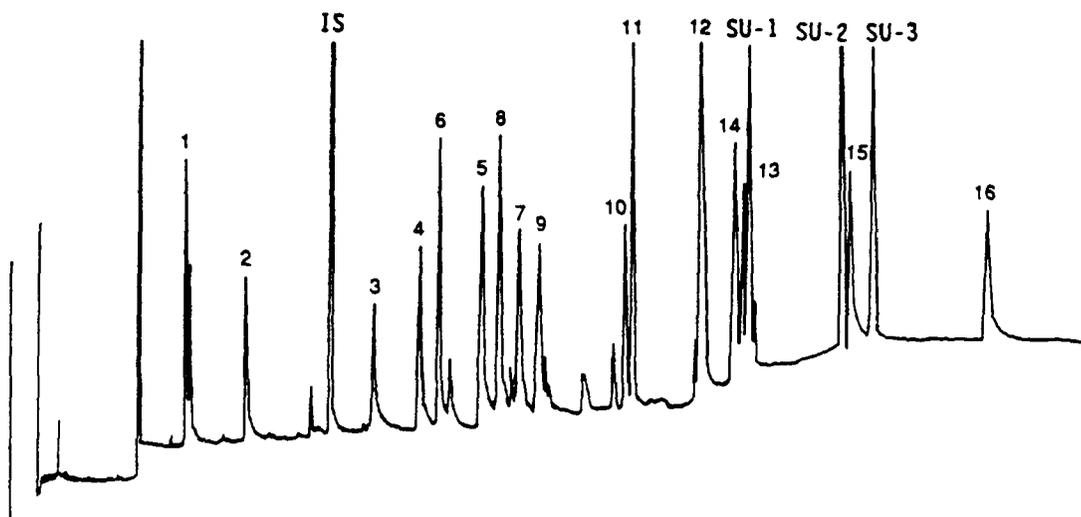
^a The number of determinations was 3. The values given in parentheses are the percent relative standard deviations of the average recoveries. All samples were subjected to Florisil cartridge cleanup.

^b The estuarine sediment extract (Florisil, Fraction 1) was subjected to sulfur cleanup (Method 3660 with tetrabutylammonium sulfite reagent).

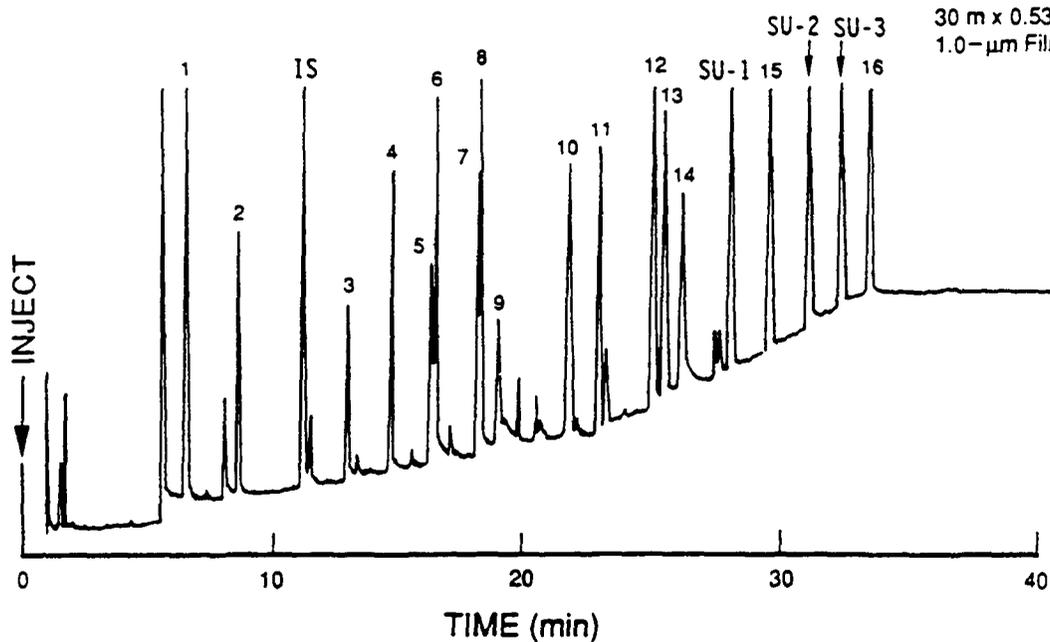
^c Not able to determine because of matrix interferant.

Figure 1

DB-5
30 m x 0.53 mm ID
1.5- μ m Film

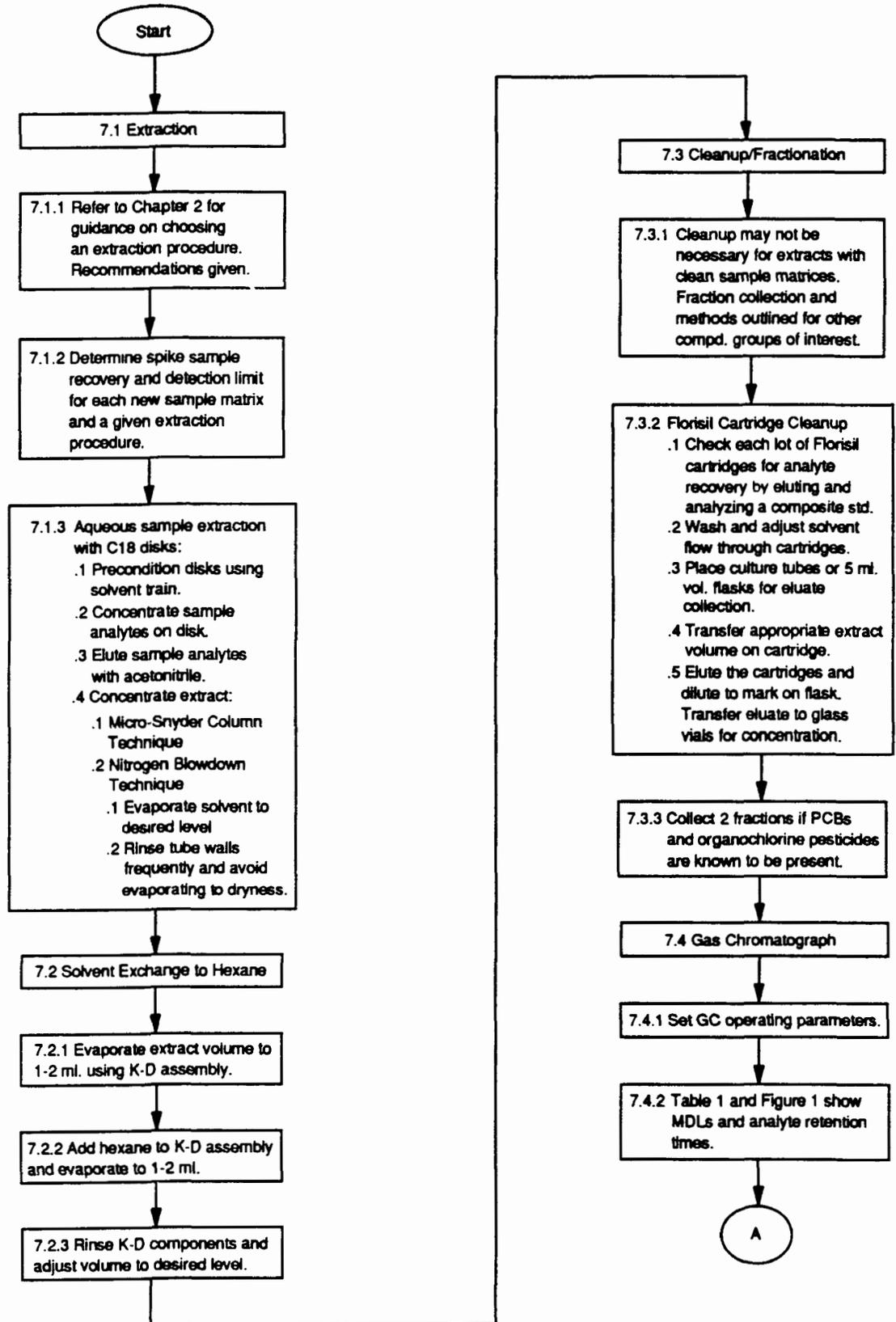


DB-1701
30 m x 0.53 mm ID
1.0- μ m Film

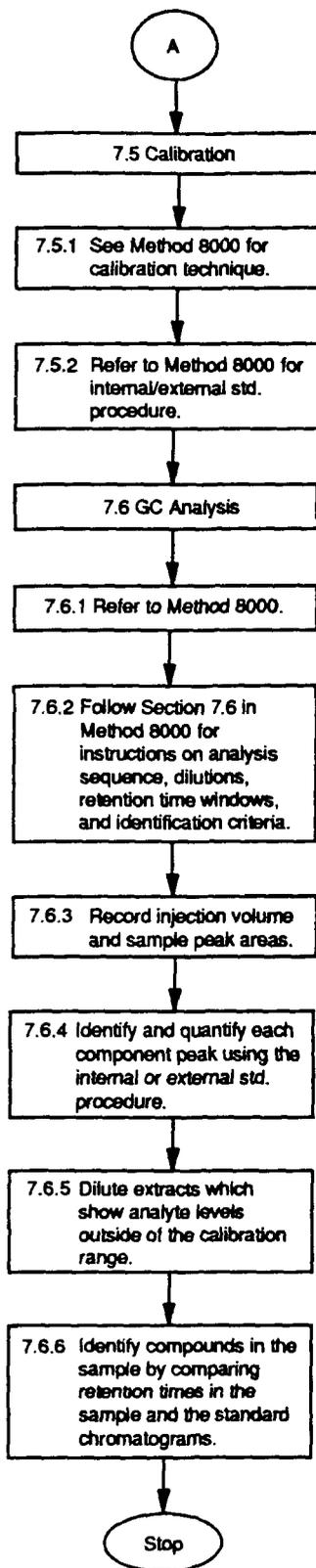


GC/ECD chromatograms of a composite phthalate esters standard (concentration 10 ng/ μ L per compound) analyzed on a DB-5 and a DB-1701 fused-silica open tubular column. Temperature program: 150°C (0.5 min hold) to 220°C at 5°C/min, then to 275°C (13 min hold) at 3°C/min.

METHOD 8061
 PHTHALATE ESTERS BY CAPILLARY GAS CHROMATOGRAPHY
 WITH ELECTRON CAPTURE DETECTION (GC/ECD)



METHOD 8061
(CONTINUED)



METHOD 8070

NITROSAMINES

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of certain nitrosamines. The following parameters can be determined by this method:

Parameter	CAS No.
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7

1.2 This is a gas chromatographic (GC) method applicable to the determination of the parameters listed above in municipal and industrial discharges. When this method is used to analyze unfamiliar samples for any or all of the compounds above, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Method 8270 provides gas chromatograph/mass spectrometer (GC/MS) conditions appropriate for the qualitative and quantitative confirmation of results for N-nitrosodi-n-propylamine. In order to confirm the presence of N-nitrosodi-phenylamine, the cleanup procedure specified in Step 7.3.3 or 7.3.4 must be used. In order to confirm the presence of N-nitrosodimethylamine by GC/MS, chromatographic column 1 of this method must be substituted for the column recommended in Method 8270. Confirmation of these parameters using GC-high resolution mass spectrometry or a Thermal Energy Analyzer is also recommended practice.

1.3 The method detection limit (MDL) for each parameter is listed in Table 1. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix. Table 2 lists the Practical Quantitation Limits (PQLs) for various matrices.

1.4 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures.

1.5 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets

should also be made available to all personnel involved in the chemical analysis.

1.6 These nitrosamines are known carcinogens. Therefore, utmost care must be exercised in the handling of these materials. Nitrosamine reference standards and standard solutions should be handled and prepared in a ventilated glove box within a properly ventilated room.

1.7 N-Nitrosodiphenylamine is reported to undergo transnitrosation reactions. Care must be exercised in the heating or concentrating of solutions containing this compound in the presence of reactive amines.

2.0 SUMMARY OF METHOD

2.1 A measured volume of sample, approximately one liter, is solvent extracted with methylene chloride using a separatory funnel. The methylene chloride extract is washed with dilute HCl to remove free amines, dried, and concentrated to a volume of 10 mL or less. Gas chromatographic conditions are described which permit the separation and measurement of the compounds in the extract after it has been exchanged to methanol.

2.2 Method 8070 provides gas chromatographic conditions for the detection of ppb levels of nitrosamines. Prior to use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by a nitrogen-phosphorus detector (NPD) or a Thermal Energy Analyzer and the reactive Hall detector.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality being sampled. The cleanup procedures (Methods 3610 or 3620) can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the MDL listed in Table 1.

3.3 Nitrosamines contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no nitrosamine residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because nitrosamines are commonly used as plasticizers and are easily extracted from plastic materials. Serious nitrosamine contamination may result at any time if consistent quality control is not practiced.

3.4 The sensitive and selective Thermal Energy Analyzer and the reductive Hall detector may be used in place of the nitrogen-phosphorus detector when

interferences are encountered. The Thermal Energy Analyzer offers the highest selectivity of the non-mass spectrometric detectors.

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

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

4.0 APPARATUS AND MATERIALS

4.1 Kuderna-Danish (K-D) apparatus

4.1.1 Concentrator tube - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

4.1.2 Evaporation flask - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

4.1.3 Snyder column - Three ball macro (Kontes K-503000-0121 or equivalent).

4.1.4 Snyder column - Two ball micro (Kontes K-569001-0219 or equivalent).

4.2 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

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

4.4 Balance - Analytical, capable of accurately weighing 0.0001 g.

4.5 Vials - 10- to 15-mL, amber glass with Teflon lined screw-cap.

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

4.6.1 Column 1 - 1.8 m x 4 mm i.d. Pyrex glass, packed with Chromosorb W AW, (80/100 mesh) coated with 10% Carbowax 20 M/2% KOH or equivalent. This column was used to develop the method performance

statements in Section 9.0. Guidelines for the use of alternate column packings are provided in Step 7.3.2.

4.6.2 Column 2 - 1.8 m x 4 mm i.d. Pyrex glass, packed with Supelcoport (100/120 mesh) coated with 10% SP-2250.

4.6.3 Detector - Nitrogen-Phosphorus, reductive Hall or Thermal Energy Analyzer. These detectors have proven effective in the analysis of wastewaters for the parameters listed in the scope. A nitrogen-phosphorus detector was used to develop the method performance statements in Section 9.0. Guidelines for the use of alternate detectors are provided in Step 7.3.2.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

5.3 Methanol, CH₃OH. Pesticide quality or equivalent.

5.4 Stock standard solutions (1000 mg/L) - Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.4.1 Prepare stock standard solutions by accurately weighing 0.1000 ± 0.0010 g of pure material. Dissolve the material in pesticide quality methanol and dilute to volume in a 100-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into bottles with Teflon lined screw-caps. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after six months, or sooner if comparison with check standards indicate a problem.

5.5 Calibration standards - A minimum of five levels should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method

detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used) - To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Step 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards - The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with one or two surrogates (e.g. nitrosamines are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Step 5.3.1.1, details instructions on the preparation of base/neutral surrogates. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Step 4.1. Extracts must be stored at 4°C and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to methanol. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of methanol, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of methanol to prewet the Snyder column. Place the 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 liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Step 7.1.2.3. If cleanup is needed, proceed to Step 7.1.2.4.

7.1.2.3 If cleanup of the extract is not required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methanol. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon lined screw-cap. Proceed with gas chromatographic analysis.

7.1.2.4 If cleanup of the extract is required, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of methylene chloride. A 5-mL syringe is recommended for this operation. Add a clean boiling chip to the concentrator tube and attach a two ball micro-Snyder column. Prewet the column by adding about 0.5 mL of methanol to the top. Place the micro K-D apparatus on the 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 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 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

7.1.2.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of methylene chloride. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.1.3 If N-nitrosodiphenylamine is to be measured by gas chromatography, the analyst must first use a cleanup column to eliminate diphenylamine interference (Methods 3610 or 3620). If N-nitrosodiphenylamine is of no interest, the analyst may proceed directly with gas chromatographic analysis (Step 7.3).

7.2 Cleanup

7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedure recommended in this method has been used for the analysis of various clean waters and industrial effluents. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest is no less than 85%. Diphenylamine, if present in the original sample extract must be separate from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.2 Proceed with either Method 3610 or 3620, using the 2-mL methylene chloride extracts obtained from Step 7.1.2.5.

7.2.3 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.3 Gas Chromatography

7.3.1 N-nitrosodiphenylamine completely reacts to form diphenylamine at the normal operating temperatures of a GC injection port (200 to 250°C). Thus, N-nitrosodiphenylamine is chromatographed and detected as diphenylamine. Accurate determination depends on removal of diphenylamine that may be present in the original extract prior to GC (see Step 7.3).

7.3.2 Table 1 summarizes the recommended operating conditions for the gas chromatograph. This table includes retention times and MDLs that were obtained under these conditions. Examples of the parameter separations achieved by these columns are shown in Figures 1 and 2. Other packed columns, chromatographic conditions, or detectors may be used if the requirements of Step 8.2 are met. Capillary (open-tubular) columns may also be used if the relative standard deviations of responses for replicate injections are demonstrated to be less than 6% and the requirements of Step 8.2 are met.

7.4 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.4.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4.2 If cleanup is performed on the samples, the analyst should process a series of standards through the cleanup procedure and then analyze the samples by GC. This will confirm elution patterns and the absence of interferents from the reagents.

7.5 Gas chromatographic analysis

7.5.1 Refer to Method 8000. If the internal standard calibration

technique is used, add 10 uL of internal standard to the sample prior to injection.

7.5.2 Follow Step 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level check standard after each group of 10 samples in the analysis sequence.

7.5.3 Examples of GC/NPD chromatograms for nitrosamines are shown in Figures 1 and 2.

7.5.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.5.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Step 7.8 of Method 8000 for calculation equations.

7.5.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Procedures to check the GC system operation are found in Method 8000, Step 8.6.

8.2.1 The quality control (QC) reference sample concentrate (Method 8000, Step 8.6) should contain each analyte of interest at 20 ug/mL.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Step 8.10).

8.3.1 If recovery is not within limits, the following is required.

- o Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.

- o Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- o Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

9.0 METHOD PERFORMANCE

9.1 This method has been tested for linearity of recovery from spiked reagent water and has been demonstrated to be applicable for the concentration range from 4 x MDL to 1000 x MDL.

9.2 In a single laboratory (Southwest Research Institute), using spiked wastewater samples, the average recoveries presented in Table 2 were obtained. Each spiked sample was analyzed in triplicate on three separate occasions. The standard deviation of the percent recovery is also included in Table 2.

9.3 The U.S. Environmental Protection Agency is in the process of conducting an interlaboratory method study to fully define the performance of this method.

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TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Parameter	Retention Time (minutes)		Method Detection Limit (ug/L)
	Column 1	Column 2	
N-Nitrosodimethylamine	4.1	0.88	0.15
N-Nitrosodi-n-propylamine	12.1	4.2	0.46
N-Nitrosodiphenylamine ^a	12.8 ^b	6.4 ^c	0.81

Column 1 conditions: Chromosorb W AW(80/100 mesh) coated with 10% Carbowax 20 M/2% KOH packed in a 1.8 m x 4 mm i.d. glass column with helium carrier gas at a flow rate of 40 mL/min column temperature Isothermal, at 110°C, except as otherwise indicated.

Column 2 conditions: Supelcoport (100/120 mesh) coated with 10% SP-2250 packed in a 1.8 m x 4 mm i.d. glass column with helium carrier gas at a flow rate of 40 mL/min column temperature, Isothermal at 120°C, except as otherwise indicated.

^aMeasured as diphenylamine.

^bDetermined isothermally at 220°C.

^cDetermined isothermally at 210°C.

TABLE 2.
SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Average Percent Recovery	Standard Deviation %	Spike Range (ug/L)	Number of Analyses	Matrix Types
N-Nitrosodimethylamine	32	3.7	0.8	29	5
N-Nitrosodiphenylamine	79	7.1	1.2	29	5
N-Nitrosodi-n-propylamine	61	4.1	9.0	29	5

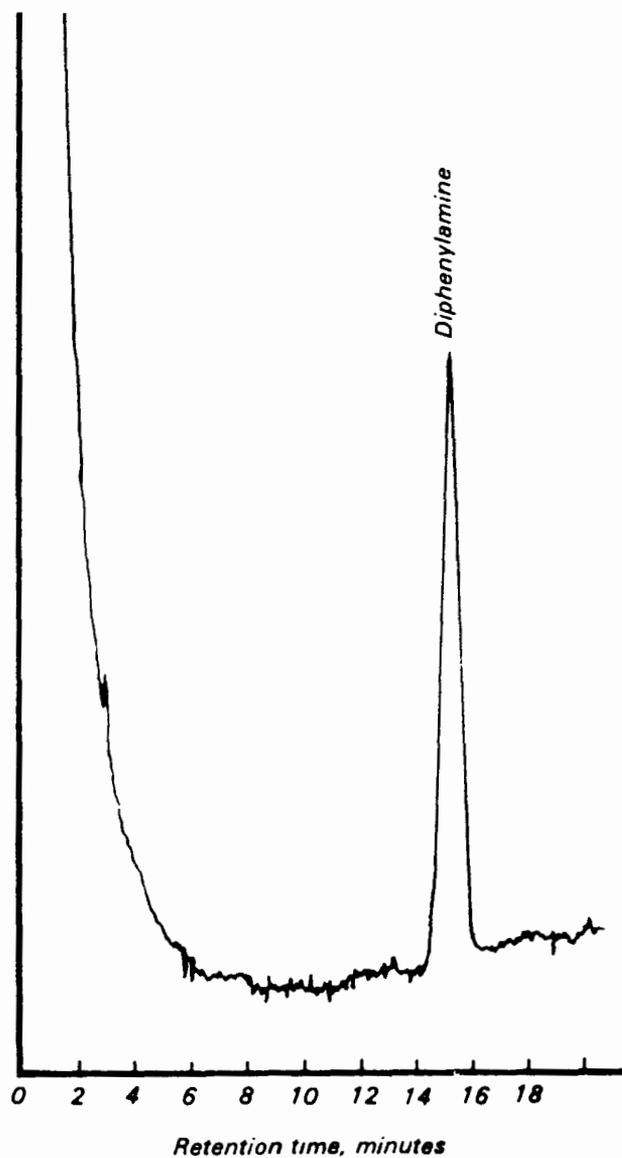
FIGURE 1.
GAS CHROMATOGRAM OF NITROSAMINES

Column: 10% Carbowax 20M + 2%
KOH on Chromosorb W-AW
Temperature: 110°
Detector: Phosphorus/Nitrogen

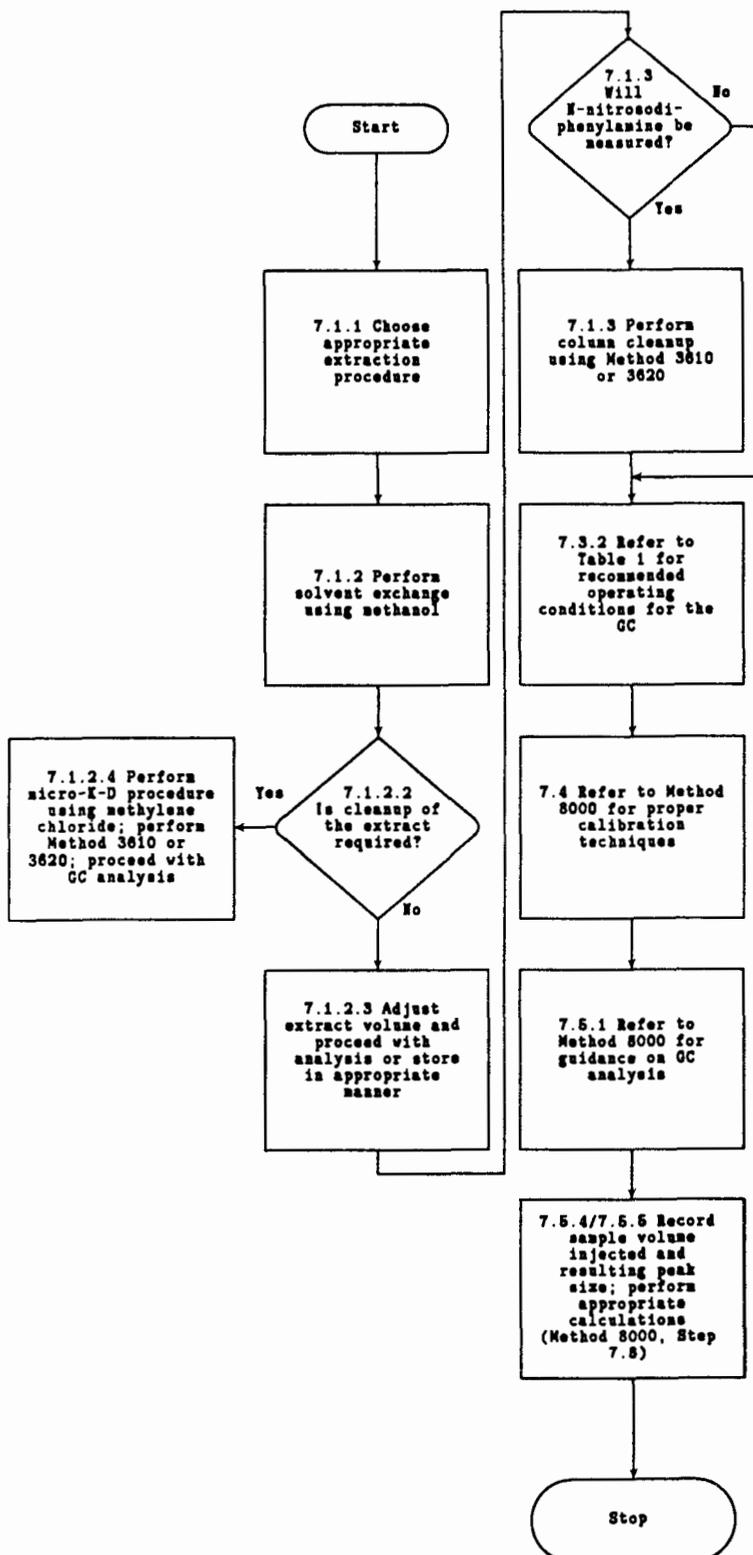


FIGURE 2.
GAS CHROMATOGRAM OF N-NITROSODIPHENYLAMINE AS DIPHENYLAMINE

Column: 10% Carbowax 20M + 2% KOH on
Chromosorb W-AW
Temperature: 220°C.
Detector: Phosphorus/Nitrogen



METHOD 8070
NITROSAMINES



METHOD 8080A

ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS
BY GAS CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). The following compounds can be determined by this method:

Compound Name	CAS No. ^a
Aldrin	309-00-2
α-BHC	319-84-6
β-BHC	319-85-7
δ-BHC	319-86-8
γ-BHC (Lindane)	58-89-9
Chlordane (technical)	12789-03-6
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dieldrin	60-57-1
Endosulfan I	959-98-8
Endosulfan II	33212-65-9
Endosulfan sulfate	1031-07-8
Endrin	72-20-8
Endrin aldehyde	7421-93-4
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
4,4'-Methoxychlor	72-43-5
Toxaphene	8001-35-2
Aroclor-1016	12674-11-2
Aroclor-1221	1104-28-2
Aroclor-1232	11141-16-5
Aroclor-1242	53469-21-9
Aroclor-1248	12672-29-6
Aroclor-1254	11097-69-1
Aroclor-1260	11096-82-5

a Chemical Abstract Services Registry Number.

1.2 Table 1 lists the method detection limit for each compound in organic-free reagent water. Table 2 lists the estimated quantitation limit (EQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2 to 5 μ L sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or an electrolytic conductivity detector (HECD).

2.2 The sensitivity of Method 8080 usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500, 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph

4.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

4.1.2 Columns

4.1.2.1 Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.2.2 Column 2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 m x 4 mm ID glass column or equivalent.

4.1.3 Detectors: Electron capture (ECD) or electrolytic conductivity detector (HECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 Concentrator tube: 10 mL, graduated (Kontes K-570050-1025 or equivalent). A ground-glass stopper is used to prevent evaporation of extracts.

4.2.2 Evaporation flask: 500 mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

4.2.3 Snyder column: Three ball macro (Kontes K-503000-0121 or equivalent).

4.2.4 Snyder column: Two ball micro (Kontes K-569001-0219 or equivalent).

4.2.5 Springs - 1/2 inch (Kontes K-662750 or equivalent).

4.3 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.4 Water bath: Heated, with concentric ring cover, capable of temperature control ($\pm 5^{\circ}\text{C}$). The bath should be used in a hood.

4.5 Volumetric flasks, Class A: sizes as appropriate with ground-glass stoppers.

4.6 Microsyringe: 10 μL .

4.7 Syringe: 5 mL.

4.8 Vials: Glass, 2, 10, and 20 mL capacity with Teflon-lined screw caps or crimp tops.

4.9 Balances: Analytical, 0.0001 g and Top loading, 0.01 g.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Solvents

5.3.1 Hexane, C_6H_{14} - Pesticide quality or equivalent.

5.3.2 Acetone, CH_3COCH_3 - Pesticide quality or equivalent.

5.3.3 Toluene, $C_6H_5CH_3$ - Pesticide quality or equivalent.

5.3.4 Isooctane, $(CH_3)_3CCH_2CH(CH_3)_2$ - Pesticide quality or equivalent.

5.4 Stock standard solutions:

5.4.1 Prepare stock standard solutions at a concentration of 1000 mg/L by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10 mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.4.2 Transfer the stock standard solutions into vials with Teflon-lined screw caps or crimp tops. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.4.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.5 Calibration standards: Calibration standards at a minimum of five concentrations for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.6 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.6.1 Prepare calibration standards at a minimum of five concentrations for each analyte of interest as described in Section 5.5.

5.6.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.6.3 Analyze each calibration standard according to Section 7.0.

5.7 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and organic-free reagent water blank with pesticide surrogates. Because GC/ECD data are much more subject to interference than GC/MS, a secondary surrogate is to be used when sample interference is apparent. Two surrogate standards (tetrachloro-m-xylene (TCMX) and decachlorobiphenyl) are added to each sample; however, only one need be calculated for recovery. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500 indicates the proper procedure for preparing these surrogates.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to this chapter, Organic Analytes, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Extraction:

7.1.1 Refer to Chapter Two for guidance on choosing the appropriate extraction procedure. In general, water samples are extracted at a neutral, or as is, pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using Method 3540, 3541, or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent must be exchanged to hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange is performed as follows.

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 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. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store

refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 Column 1:

Carrier gas (5% methane/95% argon) flow rate: 60 mL/min
Column temperature: 200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 Column 2:

Carrier gas (5% methane/95% argon) flow rate: 60 mL/min
Column temperature: 200°C isothermal

When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow to provide sufficient resolution for accurate quantitation of the analytes. This will normally result in a retention time of 10 to 12 minutes for 4,4'-DDT, depending on the packed column used.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-concentration standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to injection.

7.4.2 Method 8000 provides instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

NOTE: A 72 hour sequence is not required with this method.

7.4.3 Examples of GC/ECD chromatograms for various pesticides and PCBs are shown in Figures 1 through 5.

7.4.4 Prime the column as per Section 7.3.2.

7.4.5 DDT and endrin are easily degraded in the injection port if the injection port or front of the column is dirty. This is the result of buildup of high boiling residue from sample injection. Check for degradation problems by injecting a mid-concentration standard containing only 4,4'-DDT and endrin. Look for the degradation products of 4,4'-DDT (4,4'-DDE and 4,4'-DDD) and endrin (endrin ketone and endrin aldehyde). If degradation of either DDT or endrin exceeds 20%, take corrective action before proceeding with calibration, by following the GC system maintenance outlined in of Method 8000. Calculate percent breakdown as follows:

$$\begin{array}{l} \text{\% breakdown} \\ \text{for 4,4'-DDT} \end{array} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\begin{array}{l} \text{\% breakdown} \\ \text{for Endrin} \end{array} = \frac{\text{Total endrin degradation peak area} \\ \text{(endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin +} \\ \text{endrin aldehyde + endrin ketone)}} \times 100$$

7.4.6 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.7 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each component peak in the sample chromatogram which corresponds to the compounds used for calibration purposes.

7.4.8 If peak detection and identification are prevented due to interferences, the hexane extract may need to undergo cleanup using Method 3620. The resultant extract(s) may be analyzed by GC directly or may undergo further cleanup to remove sulfur using Method 3660.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, followed by, if necessary, Method 3660, using the 10 mL hexane extracts obtained from Section 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous sections and in Method 8000.

7.5.3 If only PCBs are to be measured in a sample, the sulfuric acid/permanganate cleanup (Method 3665), followed by Silica Cleanup (Method 3630) or Florisil Cleanup (Method 3620), is recommended.

7.6 Calculations (excerpted from U.S. FDA, PAM):

7.6.1 Calculation of Certain Residues: Residues which are mixtures of two or more components present problems in measurement. When they are found together, e.g., toxaphene and DDT, the problem of quantitation becomes even more difficult. In the following sections suggestions are offered for handling toxaphene, chlordane, PCB, DDT, and BHC. A 10% DC-200 stationary phase column was used to obtain the chromatograms in Figures 6-9.

7.6.2 Toxaphene: Quantitative calculation of toxaphene or Strobane is difficult, but reasonable accuracy can be obtained. To calculate toxaphene on GC/ECD: (a) adjust sample size so that toxaphene major peaks are 10-30% full-scale deflection (FSD); (b) inject a toxaphene standard that is estimated to be within ± 10 ng of the sample; (c) construct the baseline of standard toxaphene between its extremities; and (d) construct the baseline under the sample, using the distances of the peak troughs to baseline on the standard as a guide (Figures 7, 8, and 9). This procedure is made difficult by the fact that the relative heights and widths of the peaks in the sample will probably not be identical to the standard. A toxaphene standard that has been passed through a Florisil column will show a shorter retention time for peak X and an enlargement of peak Y.

7.6.3 Toxaphene and DDT: If DDT is present, it will superimpose itself on toxaphene peak V. To determine the approximate baseline of the DDT, draw a line connecting the trough of peaks U and V with the trough of peaks W and X and construct another line parallel to this line which will just cut the top of peak W (Figure 61). This procedure was tested with ratios of standard toxaphene-DDT mixtures from 1:10 to 2:1 and the results of added and calculated DDT and toxaphene by the "parallel lines" method of baseline construction were within 10% of the actual values in all cases.

7.6.3.1 A series of toxaphene residues have been calculated using total peak area for comparison to the standard and also using area of the last four peaks only in both sample and standard. The agreement between the results obtained by the two methods justifies the use of the latter method for calculating toxaphene in a sample where the early eluting portion of the toxaphene chromatogram is interfered with by other substances.

7.6.3.2 The baseline for methoxychlor superimposed on toxaphene (Figure 8b) was constructed by overlaying the samples on a toxaphene standard of approximately the same concentration (Figure 8a) and viewing the charts against a lighted background.

7.6.4 Chlordane is a technical mixture of at least 11 major components and 30 or more minor ones. Gas chromatography-mass spectrometry and nuclear magnetic resonance analytical techniques have been applied to the elucidation of the chemical structures of the many chlordane constituents. Figure 9a is a chromatogram of standard chlordane. Peaks E and F are responses to trans- and cis-chlordane, respectively. These are the two major components of technical chlordane, but the exact percentage of each in the technical material is not completely

defined and is not consistent from batch to batch. Other labelled peaks in Figure 9a are thought to represent: A, monochlorinated adduct of pentachlorocyclopentadiene with cyclopentadiene; B, coelution of heptachlor and α -chlordene; C, coelution of β -chlordene and γ -chlordene; D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of constituents from the technical chlordane, plant and/or animal metabolites, and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, a metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.4.5 To measure the total area of the chlordane chromatogram, proceed as in Section 7.6.2 on toxaphene. Inject an amount of technical chlordane standard which will produce a chromatogram in which peaks E and F are approximately the same size as those in the sample chromatograms. Construct the baseline beneath the standard from the beginning of peak A to the end of peak F as shown in Figure 9a. Use the distance from the trough between peaks E and F to the baseline in the chromatogram of the standard to construct the baseline in the chromatogram of the sample. Figure 9b shows how the presence of toxaphene causes the baseline under chlordane to take an upward angle. When the size of peaks E and F in standard and sample chromatograms are the same, the distance from the trough of the peaks to the baselines should be the same. Measurement of chlordane area should be done by total peak area if possible.

NOTE: A comparison has been made of the total peak area integration method and the addition of peak heights method for several samples containing chlordane. The peak heights A, B, C, D, E, and F were measured in millimeters from peak maximum of each to the baseline constructed under the total chlordane area and were then added together. These results obtained by the two techniques are too close to ignore this method of "peak height addition" as a means of calculating chlordane. The technique has inherent difficulties because not all the peaks are symmetrical and not all are present in the same ratio in standard and in sample. This method does offer a means of calculating results if no means of measuring total area is practical.

7.6.5 Polychlorinated biphenyls (PCBs): Quantitation of residues of PCB involves problems similar to those encountered in the quantitation of toxaphene, Strobane, and chlordane. In each case, the chemical is made up of numerous compounds. So the chromatograms are multi-peak. Also in each case, the chromatogram of the residue may not match that of the standard.

7.6.5.1 Mixtures of PCBs of various chlorine contents were sold for many years in the U.S. by the Monsanto Co. under the tradename Aroclor (1200 series and 1016). Though these Aroclors are no longer marketed, the PCBs remain in the environment and are sometimes found as residues in foods, especially fish.

7.6.5.2 PCB residues are quantitated by comparison to one or more of the Aroclor materials, depending on the chromatographic pattern of the residue. A choice must be made as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the residue. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material.

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area or height of peaks from appropriate Aroclor(s) reference materials. Measure total area or

height response from common baseline under all peaks. Use only those peaks from the sample that can be attributed to chlorobiphenyls. These peaks must also be present in the chromatogram of the reference materials. Mixtures of Aroclors may be required to provide the best match of GC patterns of sample and reference.

7.6.6 DDT: DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and DDD are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride): Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α -, γ -, and δ -isomers and 14 weeks for the β -isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β -isomer.

7.6.7.2 Individual isomers (α , β , γ , and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α -, γ -, and δ -isomers show equal electron affinity. β -BHC shows a much weaker electron affinity compared to the other isomers.

7.6.7.3 Quantitate each isomer (α , β , γ , and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Quality control required to evaluate the GC system operation is found in Method 8000.

8.2.1 The quality control check sample concentrate (Method 8000) should contain each single-component parameter of interest at the following concentrations in acetone or other water miscible solvent: 4,4'-DDD, 10 mg/L; 4,4'-DDT, 10 mg/L; endosulfan II, 10 mg/L; endosulfan sulfate, 10 mg/L; endrin, 10 mg/L; and any other single-component

pesticide, 2 mg/L. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 mg/L in acetone.

8.2.2 Table 3 indicates the calibration and QC acceptance criteria for this method. Table 4 gives method accuracy and precision as functions of concentration for the analytes of interest. The contents of both Tables should be used to evaluate a laboratory's ability to perform and generate acceptable data by this method.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000).

8.3.1 If recovery is not within limits, the following is required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration".

8.4 GC/MS confirmation: Any compounds confirmed by two columns may also be confirmed by GC/MS if the concentration is sufficient for detection by GC/MS as determined by the laboratory generated detection limits.

8.4.1 The GC/MS would normally require a minimum concentration of 10 ng/ μ L in the final extract, for each single-component compound.

8.4.2 The pesticide extract and associated blank should be analyzed by GC/MS as per Section 7.0 of Method 8270.

8.4.3 The confirmation may be from the GC/MS analysis of the base/neutral-acid extractables extracts (sample and blank). However, if the compounds are not detected in the base/neutral-acid extract even though the concentration is high enough, a GC/MS analysis of the pesticide extract should be performed.

8.4.4 A reference standard of the compound must also be analyzed by GC/MS. The concentration of the reference standard must be at a level that would demonstrate the ability to confirm the pesticides/PCBs identified by GC/ECD.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at

six concentrations. Concentrations used in the study ranged from 0.5 to 30 $\mu\text{g/L}$ for single-component pesticides and from 8.5 to 400 $\mu\text{g/L}$ for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for an electron capture detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

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TABLE 1.
GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs^a

Analyte	Retention time (min)		Method Detection limit ($\mu\text{g/L}$)
	Col. 1	Col. 2	
Aldrin	2.40	4.10	0.004
α -BHC	1.35	1.82	0.003
β -BHC	1.90	1.97	0.006
δ -BHC	2.15	2.20	0.009
γ -BHC (Lindane)	1.70	2.13	0.004
Chlordane (technical)	e	e	0.014
4,4'-DDD	7.83	9.08	0.011
4,4'-DDE	5.13	7.15	0.004
4,4'-DDT	9.40	11.75	0.012
Dieldrin	5.45	7.23	0.002
Endosulfan I	4.50	6.20	0.014
Endosulfan II	8.00	8.28	0.004
Endosulfan sulfate	14.22	10.70	0.066
Endrin	6.55	8.10	0.006
Endrin aldehyde	11.82	9.30	0.023
Heptachlor	2.00	3.35	0.003
Heptachlor epoxide	3.50	5.00	0.083
Methoxychlor	18.20	26.60	0.176
Toxaphene	e	e	0.24
PCB-1016	e	e	nd
PCB-1221	e	e	nd
PCB-1232	e	e	nd
PCB-1242	e	e	0.065
PCB-1248	e	e	nd
PCB-1254	e	e	nd
PCB-1260	e	e	nd

^aU.S. EPA. Method 617. Organochlorine Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

TABLE 2.
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQLs) FOR VARIOUS MATRICES^a

Matrix	Factor ^b
Ground water	10
Low-concentration soil by sonication with GPC cleanup	670
High-concentration soil and sludges by sonication	10,000
Non-water miscible waste	100,000

- a Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.
- b $EQL = [Method\ detection\ limit\ (Table\ 1)] \times [Factor\ (Table\ 2)]$. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 3.
QC ACCEPTANCE CRITERIA^a

Analyte	Test conc. (µg/L)	Limit for s (µg/L)	Range for \bar{x} (µg/L)	Range P, P _s (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	0.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

s = Standard deviation of four recovery measurements, in µg/L.

\bar{x} = Average recovery for four recovery measurements, in µg/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

^aCriteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.

TABLE 4.
METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION^a

Analyte	Accuracy, as recovery, x' ($\mu\text{g/L}$)	Single analyst precision, s_r' ($\mu\text{g/L}$)	Overall precision, S' ($\mu\text{g/L}$)
Aldrin	$0.81C+0.04$	$0.16\bar{x}-0.04$	$0.20\bar{x}-0.01$
α -BHC	$0.84C+0.03$	$0.13\bar{x}+0.04$	$0.23\bar{x}-0.00$
β -BHC	$0.81C+0.07$	$0.22\bar{x}+0.02$	$0.33\bar{x}-0.95$
δ -BHC	$0.81C+0.07$	$0.18\bar{x}+0.09$	$0.25\bar{x}+0.03$
γ -BHC	$0.82C-0.05$	$0.12\bar{x}+0.06$	$0.22\bar{x}+0.04$
Chlordane	$0.82C-0.04$	$0.13\bar{x}+0.13$	$0.18\bar{x}+0.18$
4,4'-DDD	$0.84C+0.30$	$0.20\bar{x}-0.18$	$0.27\bar{x}-0.14$
4,4'-DDE	$0.85C+0.14$	$0.13\bar{x}+0.06$	$0.28\bar{x}-0.09$
4,4'-DDT	$0.93C-0.13$	$0.17\bar{x}+0.39$	$0.31\bar{x}-0.21$
Dieldrin	$0.90C+0.02$	$0.12\bar{x}+0.19$	$0.16\bar{x}+0.16$
Endosulfan I	$0.97C+0.04$	$0.10\bar{x}+0.07$	$0.18\bar{x}+0.08$
Endosulfan II	$0.93C+0.34$	$0.41\bar{x}-0.65$	$0.47\bar{x}-0.20$
Endosulfan Sulfate	$0.89C-0.37$	$0.13\bar{x}+0.33$	$0.24\bar{x}+0.35$
Endrin	$0.89C-0.04$	$0.20\bar{x}+0.25$	$0.24\bar{x}+0.25$
Heptachlor	$0.69C+0.04$	$0.06\bar{x}+0.13$	$0.16\bar{x}+0.08$
Heptachlor epoxide	$0.89C+0.10$	$0.18\bar{x}-0.11$	$0.25\bar{x}-0.08$
Toxaphene	$0.80C+1.74$	$0.09\bar{x}+3.20$	$0.20\bar{x}+0.22$
PCB-1016	$0.81C+0.50$	$0.13\bar{x}+0.15$	$0.15\bar{x}+0.45$
PCB-1221	$0.96C+0.65$	$0.29\bar{x}-0.76$	$0.35\bar{x}-0.62$
PCB-1232	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1242	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1248	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1254	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$
PCB-1260	$0.91C+10.79$	$0.21\bar{x}-1.93$	$0.31\bar{x}+3.50$

x' = Expected recovery for one or more measurements of a sample containing concentration C , in $\mu\text{g/L}$.

s_r' = Expected single analyst standard deviation of measurements at an average concentration of \bar{x} , in $\mu\text{g/L}$.

S' = Expected interlaboratory standard deviation of measurements at an average concentration found of \bar{x} , in $\mu\text{g/L}$.

C = True value for the concentration, in $\mu\text{g/L}$.

\bar{x} = Average recovery found for measurements of samples containing a concentration of C , in $\mu\text{g/L}$.

Figure 1
Gas Chromatogram of Pesticides

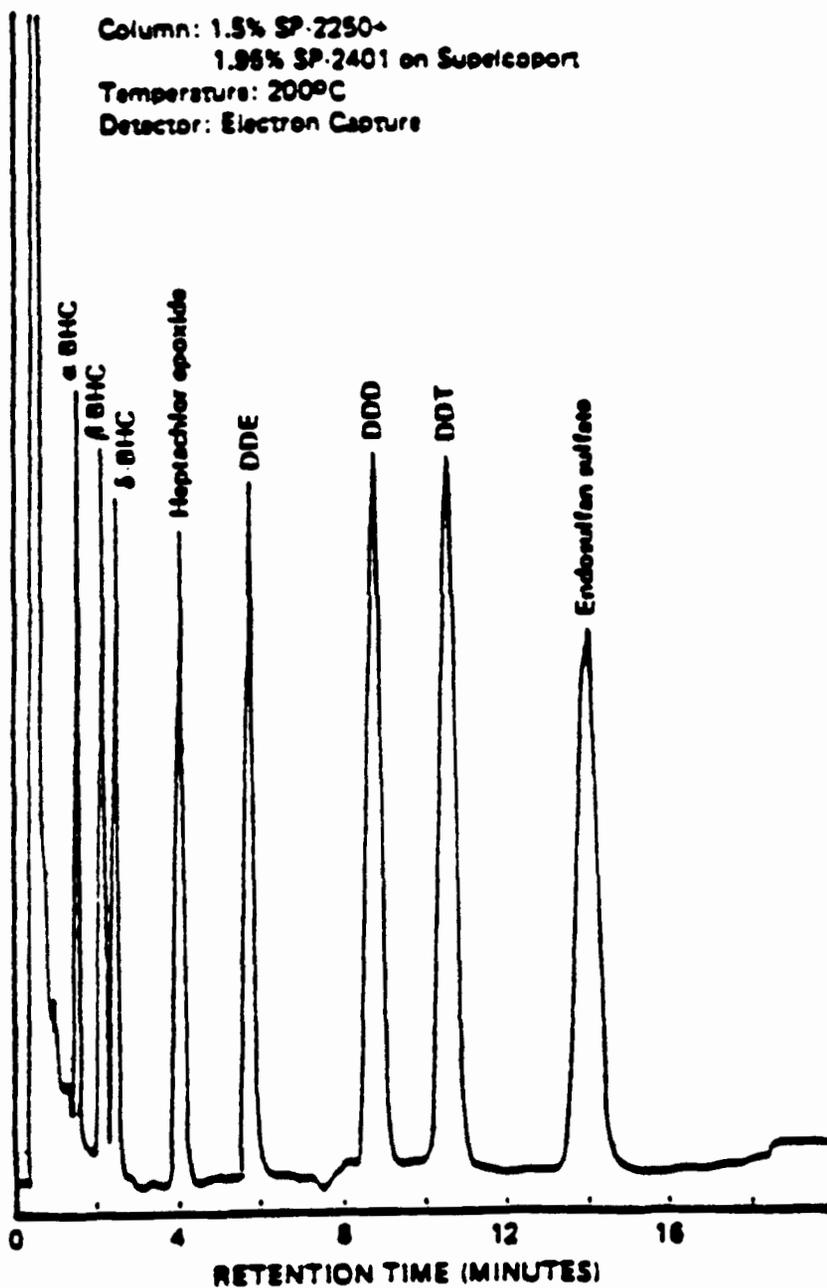


Figure 2
Gas Chromatogram of Chlordane

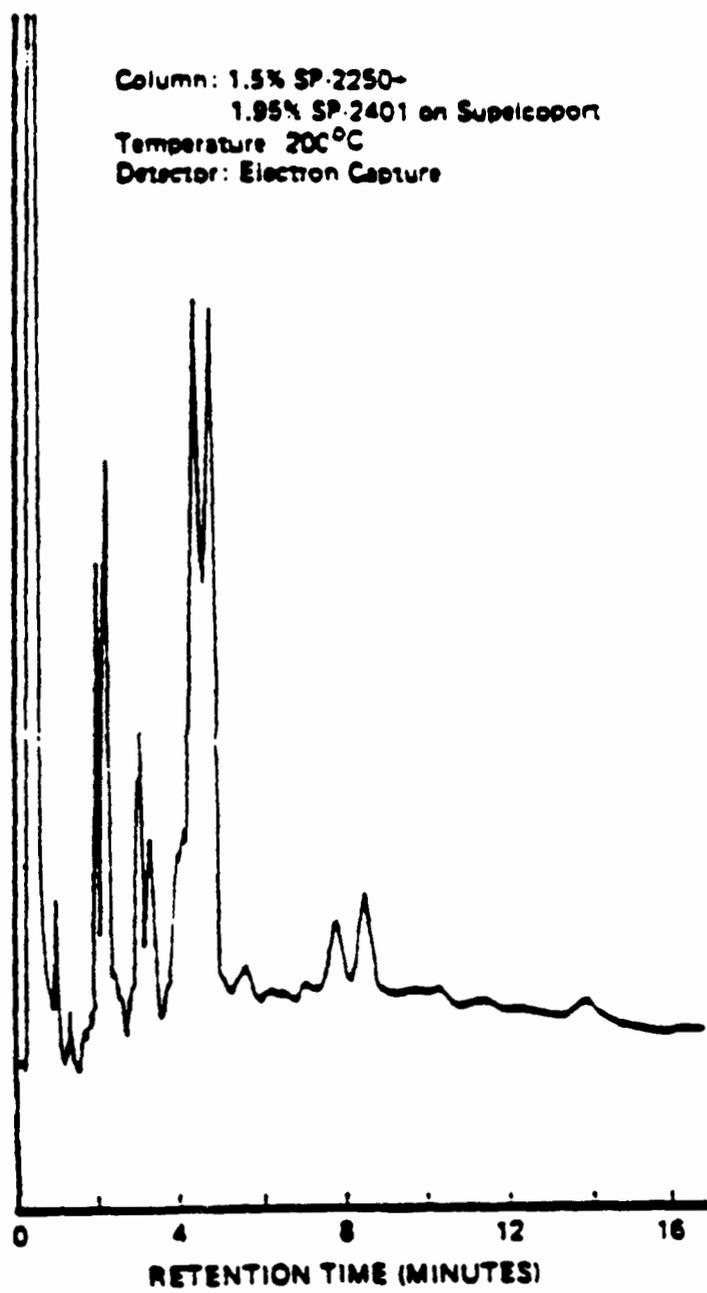


Figure 3
Gas Chromatogram of Toxaphene

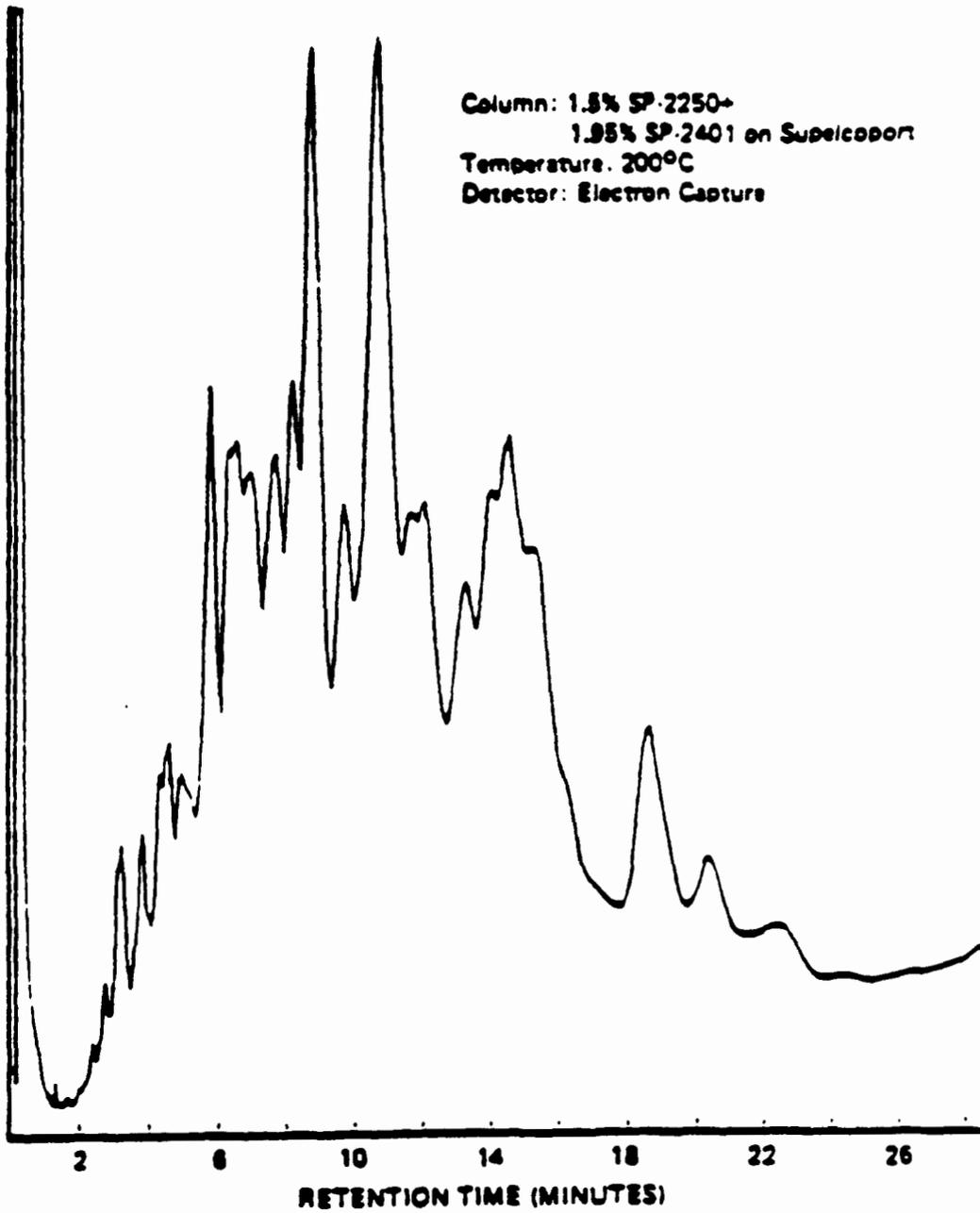


Figure 4
Gas Chromatogram of Aroclor 1254

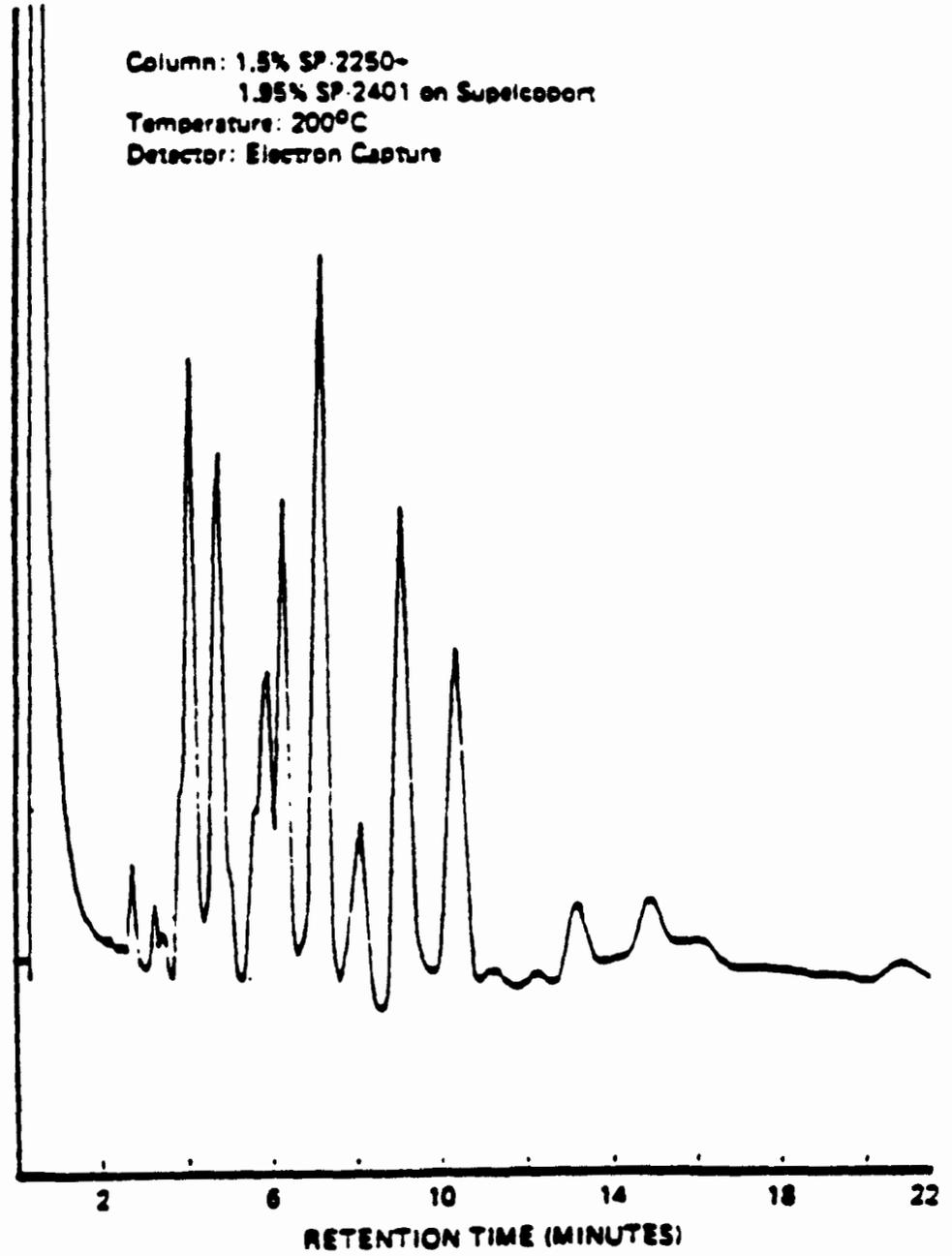


Figure 5
Gas Chromatogram of Aroclor 1260

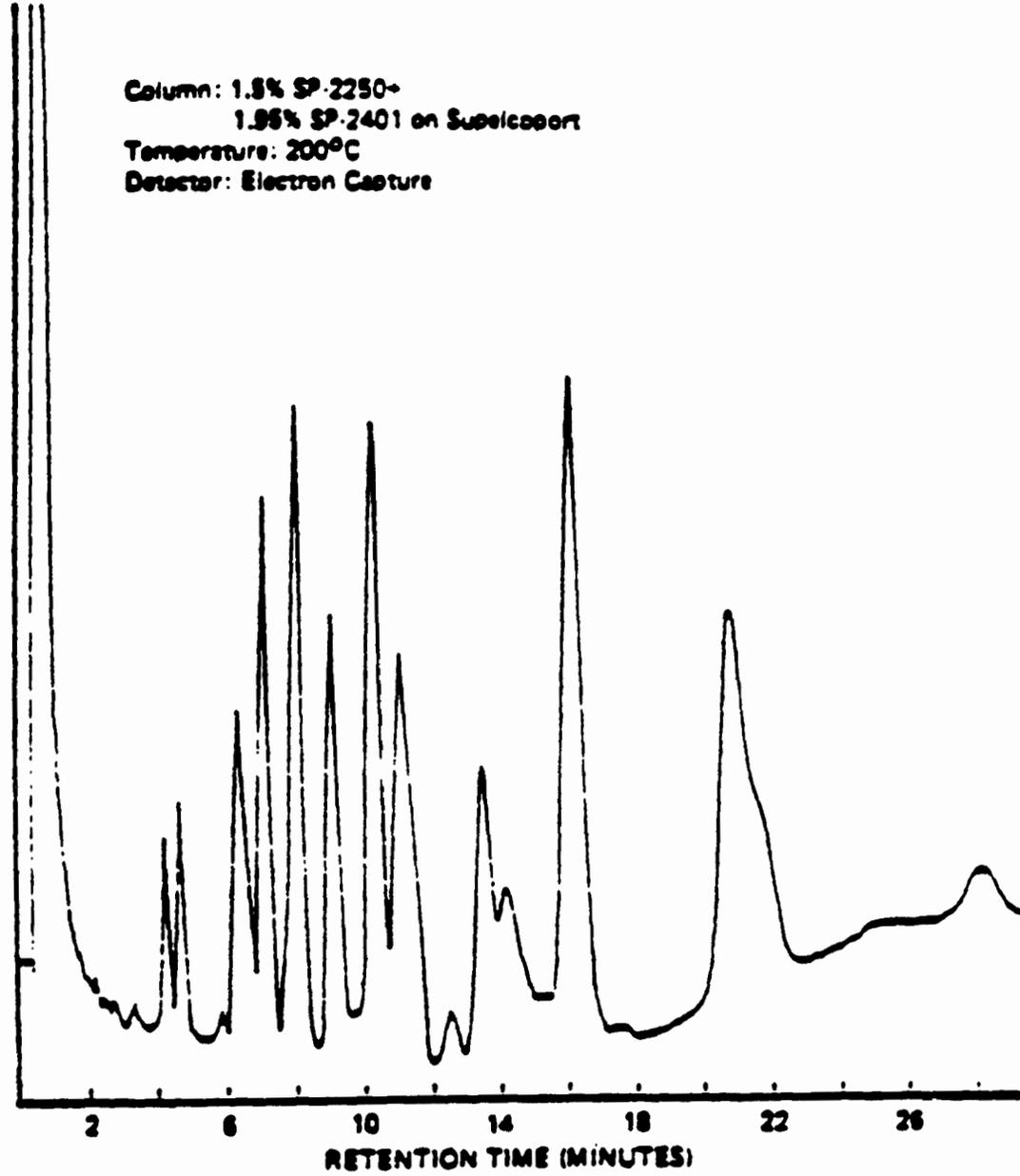


Figure 6

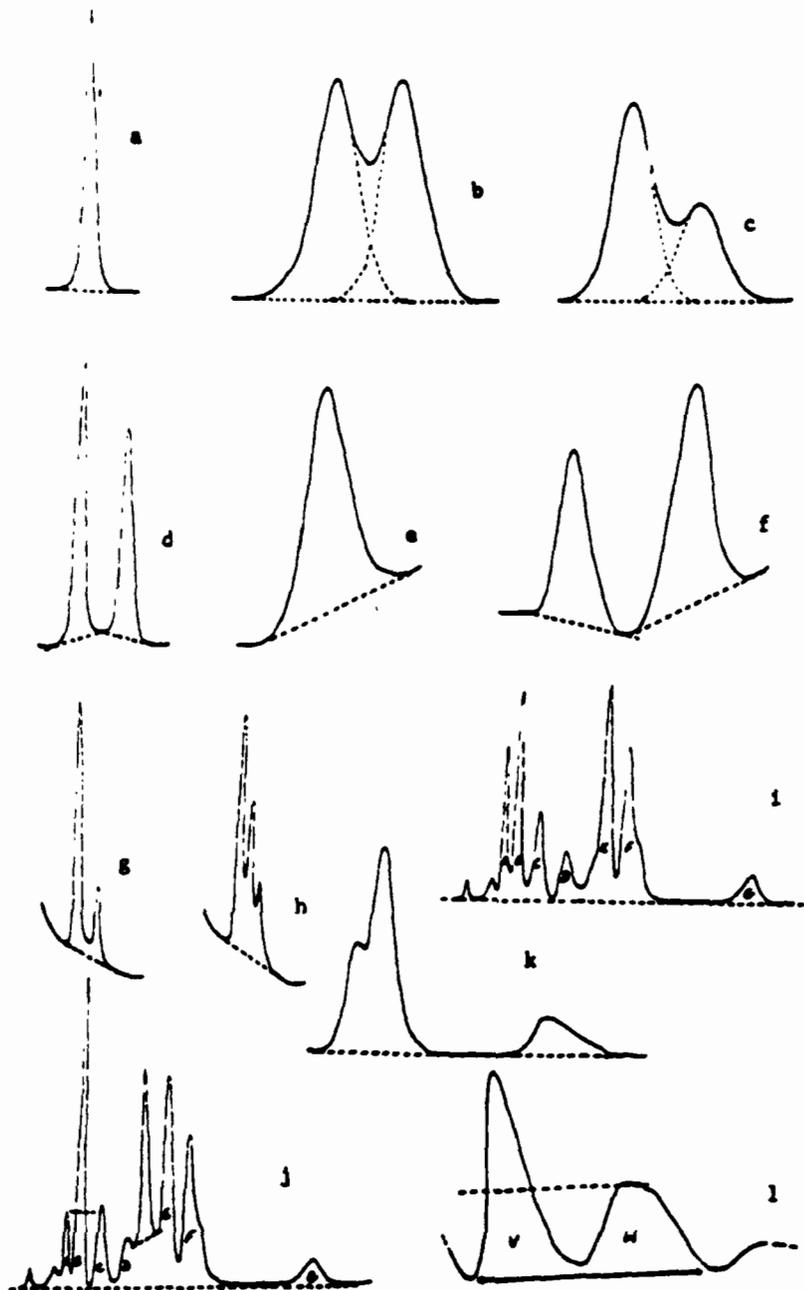


FIG. 6--Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α - and γ -BHC sloping baseline; h, α -, β -, and γ -BHC sloping baseline; i, chlordane flat baseline; j, heptachlor and heptachlor epoxide superimposed on chlordane; k, chair-shaped peaks, unsymmetrical peak; l, *p,p'*-DDT superimposed on toxaphene.

Figure 7

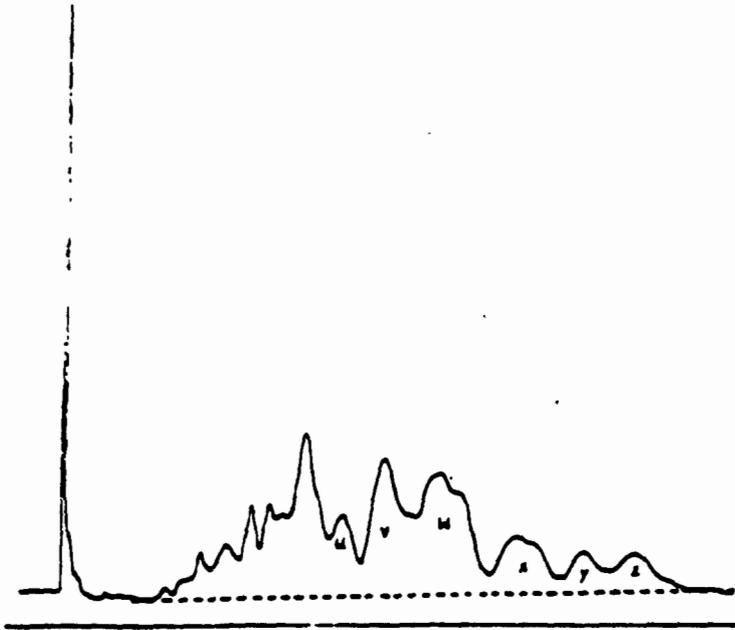


Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

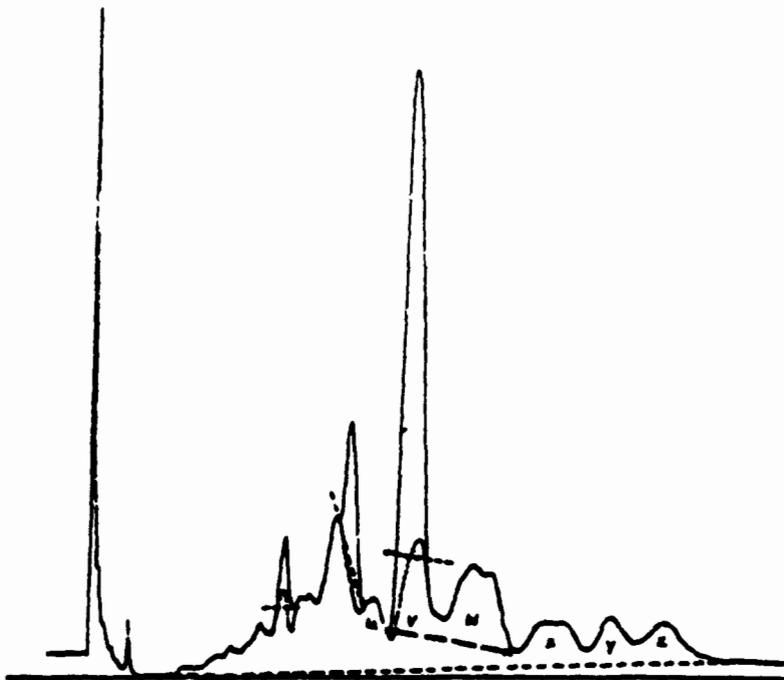


Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

Figure 8

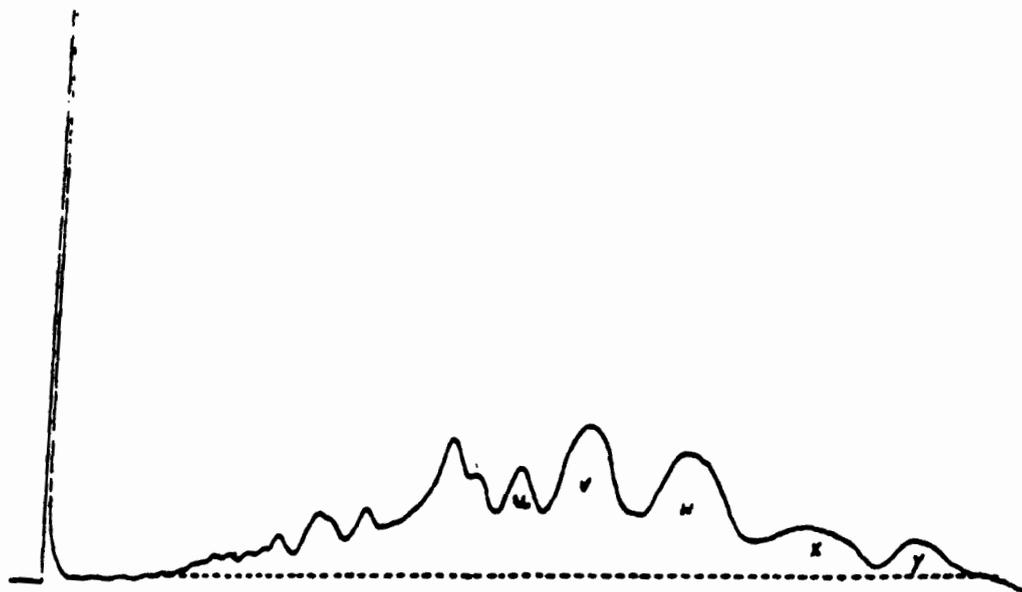


Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

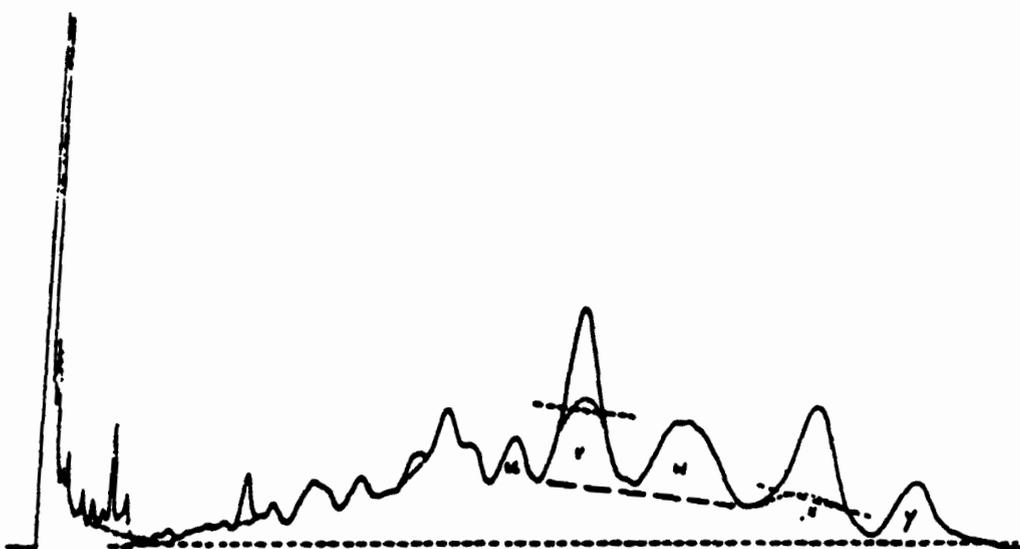


Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

Figure 9

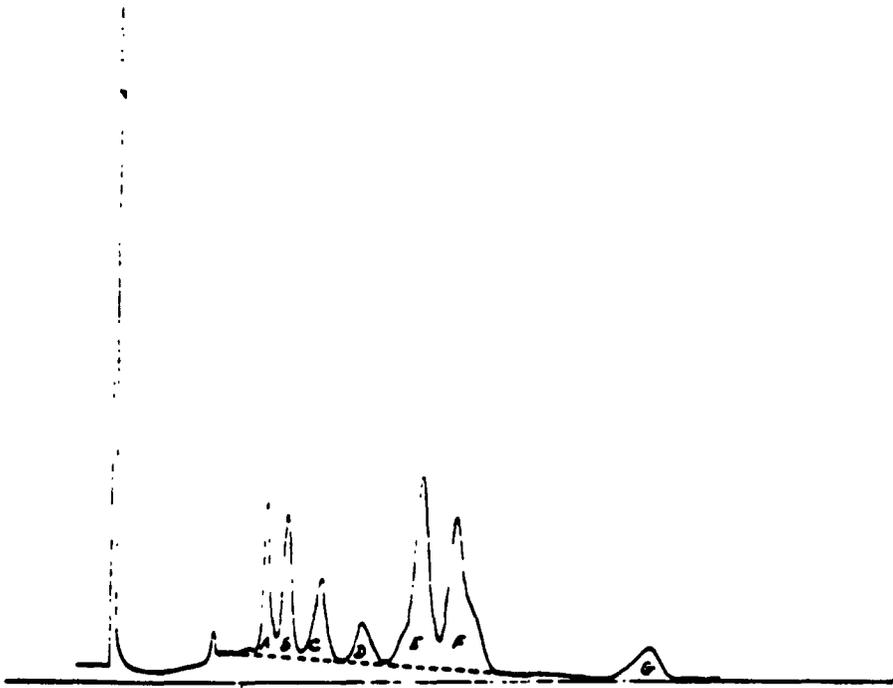


Fig. 9a--Baseline construction for multiple residues: standard chlordane.

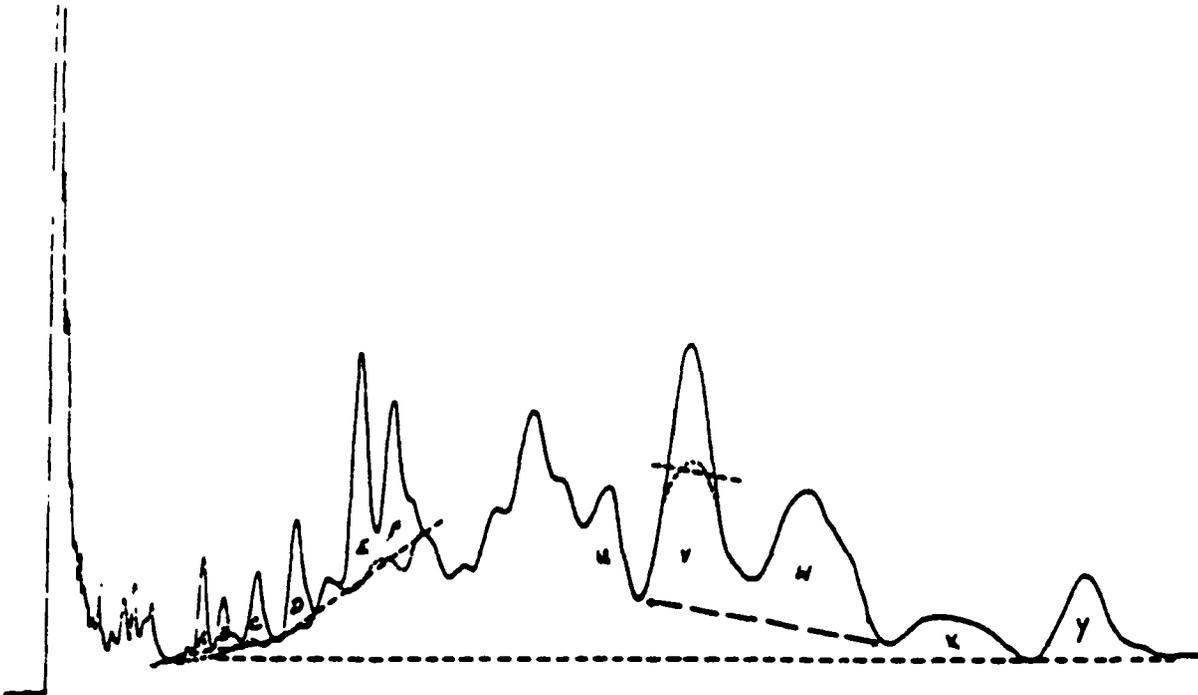


Fig. 9b--Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DOT.

METHOD 8080A
ORGANOCHLORINE PESTICIDES AND POLYCHLORINATED BIPHENYLS
BY GAS CHROMATOGRAPHY

