United States
Environmental Protection
Agency

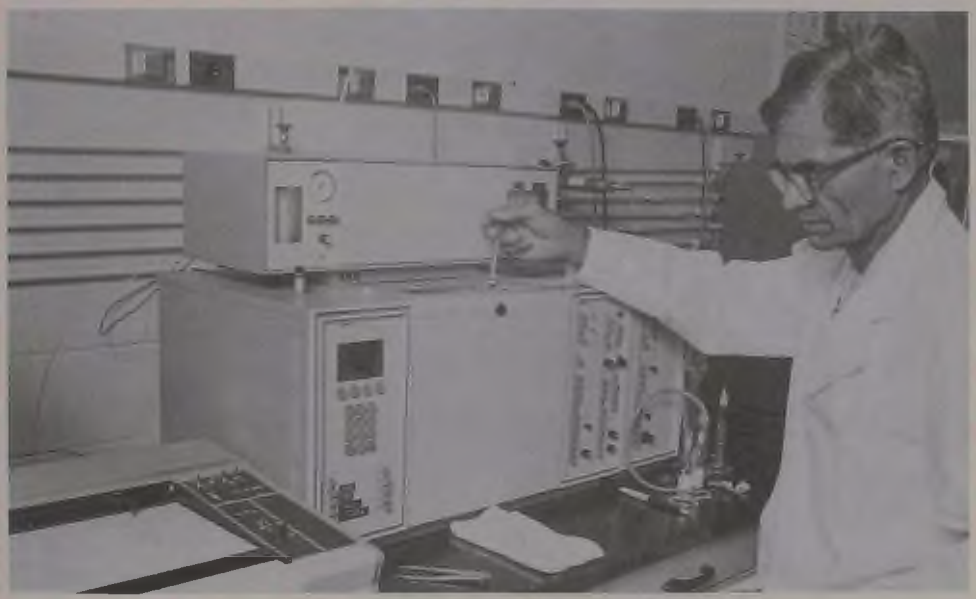
Office of Solid Waste
and Emergency Response
Washington, DC 20460

November 1986
SW-846
Third Edition

Solid Waste

Test Methods for Evaluating Solid Waste

Volume IB: Laboratory Manual Physical/Chemical Methods



ABSTRACT

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

VOLUME ONE,

SECTION B

Revision 0
Date September 1986

For sale by the Superintendent of Documents, U.S. Government Printing Office Washington, D.C. 20402

TABLE OF CONTENTS

VOLUME ONE,

SECTION A

CHAPTER THREE — METALLIC ANALYTES

VOLUME ONE,

SECTION B

VOLUME ONE,

SECTION C

VOLUME TWO

PART IV MONITORING

METHOD INDEX AND CONVERSION TABLE

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	0
1320	Six	1320	0
1330	Six	1330	0
3005	Three	3005	0
3010	Three	3010	0
3020	Three	3020	0
3040	Three	3040	0
3050	Three	3050	0
3500	Four (4.2.1)	None (new method)	0
3510	Four (4.2.1)	3510	0
3520	Four (4.2.1)	3520	0
3540	Four (4.2.1)	3540	0
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	0
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)	None (new method)	0
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	0
5040	Four (4.2.1)	3720	0
6010	Three	6010	0
7000	Three	7000	0
7020	Three	7020	0

Revision 0
Date September 1986

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	0
7080	Three	7080	0
7090	Three	7090	0
7091	Three	7091	0
7130	Three	7130	0
7131	Three	7131	0
7140	Three	7140	0
7190	Three	7190	0
7191	Three	7191	0
7195	Three	7195	0
7196	Three	7196	0
7197	Three	7197	0
7198	Three	7198	0
7200	Three	7200	0
7201	Three	7201	0
7210	Three	7210	0
7380	Three	7380	0
7420	Three	7420	0
7421	Three	7421	0
7450	Three	7450	0
7460	Three	7460	0
7470	Three	7470	0
7471	Three	7471	0
7480	Three	7480	0
7481	Three	7481	0
7520	Three	7520	0
7550	Three	7550	0
7610	Three	7610	0
7740	Three	7740	0
7741	Three	7741	0
7760	Three	7760	0
7770	Three	7770	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7840	Three	7840	0
7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
8000	Four (4.3.1)	**None (new method)**	0
8010	Four (4.3.1)	8010	0
8015	Four (4.3.1)	8015	0
8020	Four (4.3.1)	8020	0
8030	Four (4.3.1)	8030	0
8040	Four (4.3.1)	8040	0
8060	Four (4.3.1)	8060	0
8080	Four (4.3.1)	8080	0
8090	Four (4.3.1)	8090	0
8100	Four (4.3.1)	8100	0
8120	Four (4.3.1)	8120	0
8140	Four (4.3.1)	8140	0
8150	Four (4.3.1)	8150	0
8240	Four (4.3.2)	8240	0
8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
8280	Four (4.3.2)	**None (new method)**	0
8310	Four (4.3.3)	8310	0
9010	Five	9010	0
9020	Five	9020	0
9022	Five	9022	0
9030	Five	9030	0
9035	Five	9035	0
9036	Five	9036	0
9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
9066	Five	9066	0
9067	Five	9067	0
9070	Five	9070	0
9071	Five	9071	0
9080	Six	9080	0
9081	Six	9081	0
9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

CHAPTER ONE, REPRINTED

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 similarily 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, Section 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, Section 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,

f 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 corrective actions, 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 corrective actions.

1.1.8 Definitions

ACCURACY: Accuracy means the nearness of a result or the mean ($\bar{x}$) of a set of results 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.

BLANK: A blank is an artificial sample designed to monitor the introduction of artifacts into the process. For aqueous samples, reagent water is used as a blank matrix; however, a universal blank matrix does not exist for solid samples, and therefore, no matrix is used. The blank is taken through the appropriate steps of the process.
A reagent blank is an aliquot of analyte-free water or solvent analyzed with the analytical batch. Field blanks are aliquots of analyte-free water or solvents brought to the field in sealed containers and transported back to the

laboratory with the sample containers. Trip blanks and equipment blanks are two specific types of field blanks. Trip blanks are not opened in the field. They are a check on sample contamination originating from sample transport, shipping and from site conditions. Equipment blanks are opened in the field and the contents are poured appropriately over or through the sample collection device, collected in a sample container, and returned to the laboratory as a sample. Equipment blanks are a check on sampling device cleanliness.

CALIBRATION CHECK: Verification of the ratio of instrument response to analyte amount, a calibration check, is done by analyzing for analyte standards in an appropriate solvent. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

CHECK SAMPLE: A blank which has been spiked with the analyte(s) from an independent source in order to monitor the execution of the analytical method is called a check sample. The level of the spike shall be at the regulatory action level when applicable. Otherwise, the spike shall be at 5 times the estimate of the quantification limit. The matrix used shall be phase matched with the samples and well characterized: for an example, reagent grade water is appropriate for an aqueous sample.

ENVIRONMENTAL SAMPLE: 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 (treated or untreated) water 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.

MATRIX/SPIKE-DUPLICATE ANALYSIS: In matrix/spike duplicate analysis, predetermined quantities of stock solutions of certain analytes are added to a added to a sample matrix prior to sample extraction/digestion and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The relative percent difference between the samples is calculated and used to assess analytical precision. The concentration of the spike should be at the regulatory standard level or the estimated or actual method quantification limit. When the concentration of the analyte in the sample is greater than 0.1%, no spike of the analyte is necessary.

MQL: The method quantification limit (MQL) is the minimum concentration of a substance that can be measured and reported.

PRECISION: Precision means the measurement of agreement of a set of replicate results among themselves without assumption of any prior information as to the true result. 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 synonomous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REPLICATE SAMPLE: A replicate sample is a sample prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates.

STANDARD CURVE: A standard curve is a curve which plots concentrations of known analyte standard versus the instrument response to the analyte.

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, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

WATER: Reagent, analyte-free, or laboratory pure water means distilled or deionized water or Type II reagent water 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:

Reference to or incorporation of accepted sampling techniques in the sampling plan;

Procedures for documenting and justifying any field actions contrary to the QAPP;

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 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 this section shall be retained by the laboratory and shall be made available to the data requestor as appropriate. The frequencies of these procedures shall be as stated below or at least once with each analytical batch.

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 Duplicate Spike

A split/spiked field sample shall be analyzed with every analytical batch or once in twenty samples, whichever is the greater frequency. Analytes stipulated by the analytical method, by applicable regulations, or by other specific requirements must be spiked into the sample. Selection of the sample to be spiked and/or split depends on the information required and the variety of conditions within a typical matrix. In some situations, requirements of the site being sampled may dictate that the sampling team select a sample to be spiked and split based on a pre-visit evaluation or the on-site inspection. This does not preclude the laboratory's spiking a sample of its own selection as well. In other situations the laboratory may select the appropriate sample. The laboratory's selection should be guided by the objective of spiking, which is to determine the extent of matrix bias or interference on analyte recovery and sample-to-sample precision. For soil/sediment samples, spiking is performed at approximately 3 ppm and, therefore, compounds in excess of this concentration in the sample may cause interferences for the determination of the spiked analytes.

1.2.2.1.2 Blanks

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

1.2.2.1.3 Field Samples/Surrogate Compounds

Every blank, standard, and environmental sample (including matrix spike/matrix duplicate samples) 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 ±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.

1.2.2.1.4 Check Sample

Each analytical batch shall contain a check sample. The analytes employed shall be a representative subset of the analytes to be determined. The concentrations of these analytes shall approach the estimated quantification limit in the matrix of the check sample. In particular, check samples for metallic analytes shall be matched to field samples in phase and in general matrix composition.

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 (Florisil, 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.

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.

1.2.2.2.2 Column Check Sample Blank

The check blank shall be run after activating or deactivating a batch of adsorbent.

1.2.2.3 Determinations

1.2.2.3.1 Instrument Adjustment: Tuning, Alignment, etc.

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.

1.2.2.3.2 Calibration

Analytical instrumentation shall be calibrated in accordance with requirements which are specific to the instrumentation and procedures employed. Introductory Methods 7000 and 8000 and 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 reagent blank and four 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 ±10% of the original curve, a new standard shall be prepared and analyzed. If the results of the second verification are not within ±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 interferents 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 DETECTION LIMIT AND QUANTIFICATION LIMIT

The detection limit and quantification limit of analytes shall be evaluated by determining the noise level of response for each sample in the batch. If analyte is present, the noise level adjacent in retention time to the analyte peak may be used. For wave-length dispersive instrumentation, multiple determinations of digestates with no detectable analyte may be used to establish the noise level. The method of standard additions should then be used to determine the calibration curve using one digestate or extracted sample in which the analyte was not detected. The slope of the calibration curve, m, should be calculated using the following relations:

m = slope of calibration line

S_B = standard deviation of the average noise level

$MDL = KS_B/m$

For K = 3; MDL = method detection limit.

For K = 5; MQL = method quantitation limit.

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 should 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 II; 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/Duplicate Spikes (I: Form V, VI; 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 Sample (I: Form VII; O: Form VIII)

Amount spiked, and percent recovery of each compound spiked.

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

1.5.13 Detection Limit (I: Form VII; O: Form I)

Analyte detection limits with methods of estimation.

1.5.14 Results of Standard Additions (I: Form VIII)

1.5.15 Results of Serial Dilutions (I: Form IX)

1.5.16 Instrument Detection Limits (I: Form XI)

1.5.17 ICP Interelement Correction Factors and ICP Linear Ranges (when applicable) (I: Form XII, Form XIII).

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.

Date _____

COVER PAGE
INORGANIC ANALYSES DATA PACKAGE

Lab Name _____ Case No. _____

No. _____ Q.C. Report No. _____

Sample Numbers

EPA No.	Lab ID No.	EPA No.	Lab ID No.

Comments: _____

Form I

Sample No.

Date _____

INORGANIC ANALYSIS DATA SHEET

LAB NAME _____ CASE NO. _____

Lab Receipt Date _____

LAB SAMPLE ID. NO. _____ QC REPORT NO. _____

Elements Identified and Measured

Matrix: Water _____ Soil _____ Sludge _____ Other _____

ug/L or mg/kg dry weight (Circle One)

1.	Aluminum	13.	Magnesium
2.	Antimony	14.	Manganese
3.	Arsenic	15.	Mercury
4.	Barium	16.	Nickel
5.	Beryllium	17.	Potassium
6.	Cadmium	18.	Selenium
7.	Calcium	19.	Silver
8.	Chromium	20.	Sodium
9.	Cobalt	21.	Thallium
10.	Copper	22.	Vanadium
11.	Iron	23.	Zinc
12.	Lead	Precent Solids (%)	

Cyanide _____

Comments: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Form II

Q. C. Report No. _____

INITIAL AND CONTINUING CALIBRATION VERIFICATION

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

Compound	Initial Calib.[1]			Continuing Calibration[2]					
Metals:	True Value	Found	%R	True Value	Found	%R	Found	%R	Method[4]
1. Aluminum									
2. Antimony									
3. Arsenic									
4. Barium									
5. Beryllium									
6. Cadmium									
7. Calcium									
8. Chromium									
9. Cobalt									
10. Copper									
11. Iron									
12. Lead									
13. Magnesium									
14. Manganese									
15. Mercury									
16. Nickel									
17. Potassium									
18. Selenium									
19. Silver									
20. Sodium									
21. Thallium									
22. Vanadium									
23. Zinc									
Other: _____									
Cyanide									

[1] Initial Calibration Source [2] Continuing Calibration Source _____

[4] Indicate Analytical Method Used: P - ICP; A - Flame AA; F - Furnace AA

Revision 0
Date September 1986

Form III

Q. C. Report No. _____

BLANKS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS _____

Compound	Initial Calibration Blank Value	Continuing Calibration Blank Value 1	2	3	4	Preparation Blank Matrix: 1	Matrix: 2
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other:							
Cyanide							

[1] Reporting Units: aqueous, ug/L; solid mg/kg

Revision 0
Date September 1986

Form IV

Q. C. Report No. _____

ICP INTERFERENCE CHECK SAMPLE

LAB NAME _____ CASE NO. _____

Check Sample I.D. _____

DATE _____ Check Sample Source _____

Units: ug/L

Compound	Control Limits[1] Mean	Control Limits[1] Std. Dev.	True[2]	Initial Observed	Initial %R	Final Observed	Final %R
Metals:							
1. Aluminum							
2. Antimony							
3. Arsenic							
4. Barium							
5. Beryllium							
6. Cadmium							
7. Calcium							
8. Chromium							
9. Cobalt							
10. Copper							
11. Iron							
12. Lead							
13. Magnesium							
14. Manganese							
15. Mercury							
16. Nickel							
17. Potassium							
18. Selenium							
19. Silver							
20. Sodium							
21. Thallium							
22. Vanadium							
23. Zinc							
Other: _____							

[1] Mean value based on n = _____.

[2] True value of EPA ICP Interference Check Sample or contractor standard.

Revision 0
Date September 1986

Form V

Q. C. Report No. _____

SPIKE SAMPLE RECOVERY

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit %R	Spiked Sample Result (SSR)	Sample Result (SR)	Spiked Added (SA)	%R[1]
Metals:					
1. Aluminum					
2. Antimony					
3. Arsenic					
4. Barium					
5. Beryllium					
6. Cadmium					
7. Calcium					
8. Chromium					
9. Cobalt					
10. Copper					
11. Iron					
12. Lead					
13. Magnesium					
14. Manganese					
15. Mercury					
16. Nickel					
17. Potassium					
18. Selenium					
19. Silver					
20. Sodium					
21. Thallium					
22. Vanadium					
23. Zinc					
Other:					
Cyanide					

[1] %R = [(SSR - SR)/SA] x 100

"N" - out of control

"NR" - Not required

Comments: _____

Revision 0
Date September 1986

Form VI

Q. C. Report No. _____

DUPLICATES

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units _____

Matrix _____

Compound	Control Limit[1]	Sample(S)	Duplicate(D)	RPD[2]
Metals:				
1. Aluminum				
2. Antimony				
3. Arsenic				
4. Barium				
5. Beryllium				
6. Cadmium				
7. Calcium				
8. Chromium				
9. Cobalt				
10. Copper				
11. Iron				
12. Lead				
13. Magnesium				
14. Manganese				
15. Mercury				
16. Nickel				
17. Potassium				
18. Selenium				
19. Silver				
20. Sodium				
21. Thallium				
22. Vanadium				
23. Zinc				
Other:				
Cyanide				

* Out of Control

[1] To be added at a later date.

[2] RPD = [|S - D|/((S + D)/2)] x 100

NC - Non calculable RPD due to value(s) less than CRDL

Form VII

Q.C. Report No. _____

INSTRUMENT DETECTION LIMITS AND

LABORATORY CONTROL SAMPLE

LAB NAME _____ CASE NO. _____ DATE _____

LCS NO. _____

Compound	Required Detection Limits (CRDL)-ug/l	Instrument Detection Limits (IDL)-ug/l ICP/AA ID# _____	Instrument Detection Limits (IDL)-ug/l Furnace ID# _____	Lab Control Sample ug/L mg/kg (circle one) True	Found	%R
Metals:						
1. Aluminum						
2. Antimony						
3. Arsenic						
4. Barium						
5. Beryllium						
6. Cadmium						
7. Calcium						
8. Chromium						
9. Cobalt						
10. Copper						
11. Iron						
12. Lead						
13. Magnesium						
14. Manganese						
15. Mercury						
16. Nickel						
17. Potassium						
18. Selenium						
19. Silver						
20. Sodium						
21. Thallium						
22. Vanadium						
23. Zinc						
Other: _____						
Cyanide		NR	NR			

NR - Not required

Revision 0
Date September 1986

Form VIII

Q.C. Report No. _____

STANDARD ADDITION RESULTS

LAB NAME _____ CASE NO. _____

DATE _____ UNITS: ug/L

EPA Sample #	Element	Matrix	0 ADD ABS.	1 ADD CON.	1 ADD ABS.[2]	2 ADD CON.	2 ADD ABS.[2]	3 ADD CON.	3 ADD ABS.[2]	FINAL CON.[3]	r*

[2] CON is the concentration added, ABS. is the instrument readout in absorbance or concentration.

[3] Concentration as determined by MSA

*"r" is the correlation coefficient.

+ - correlation coefficient is outside of control window of 0.995.

Revision 0
Date September 1986

Form IX

Q. C. Report No. _____

ICP SERIAL DILUTIONS

LAB NAME _____ CASE NO. _____

Sample No. _____

DATE _____ Lab Sample ID No. _____

Units: ug/L

Matrix _____

Compound	Initial Sample Concentration(I)	Serial Dilution[1] Result(S)	% Difference[2]
Metals:			
1. Aluminum			
2. Antimony			
3. Arsenic			
4. Barium			
5. Beryllium			
6. Cadmium			
7. Calcium			
8. Chromium			
9. Cobalt			
10. Copper			
11. Iron			
12. Lead			
13. Magnesium			
14. Manganese			
15. Nickel			
16. Potassium			
17. Selenium			
18. Silver			
19. Sodium			
20. Thallium			
21. Vanadium			
22. Zinc			
Other:			

[1] Diluted sample concentration corrected for 1:4 dilution (see Exhibit D)

[2] Percent Difference = $\frac{|I - S|}{I} \times 100$

NR - Not Required, initial sample concentration less than 10 times IDL

NA - Not Applicable, analyte not determined by ICP

Revision 0
Date September 1986

Form X

QC Report No. _____

HOLDING TIMES

LAB NAME _____

DATE _____ CASE NO. _____

EPA Sample No.	Matrix	Date Received	Mercury Prep Date	Mercury Holding Time[1] (Days)	CN Prep Date	CN Holding Time[1] (Days)

[1]Holding time is defined as number of days between the date received and the sample preparation date.

Revision 0
Date September 1986

Form XI

INSTRUMENT DETECTION LIMITS

LAB NAME _____ DATE _____

ICP/Flame AA (Circle One) Model Number _____ Furnace AA Number _____

Element	Wavelength (nm)	IDL (ug/L)	Element	Wavelength (nm)	IDL (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes:
- Indicate the instrument for which the IDL applies with a "P" (for ICP an "A" (for Flame AA), or an "F" (for Furnace AA) behind the IDL valu
- Indicate elements commonly run with background correction (AA) with a "B" behind the analytical wavelength.
- If more than one ICP/Flame or Furnace AA is used, submit separate Forms XI-XIII for each instrument.

COMMENTS: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for Al	Ca	Fe	Mg				
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

Revision 0
Date September 1986

Form XII

ICP Interelement Correction Factors

LABORATORY _____ ICP Model Number _____

DATE _____

Analyte	Analyte Wavelength (nm)	Interelement Correction Factors for							
1. Antimony									
2. Arsenic									
3. Barium									
4. Beryllium									
5. Cadmium									
6. Chromium									
7. Cobalt									
8. Copper									
9. Lead									
10. Manganese									
11. Mercury									
12. Nickel									
13. Potassium									
14. Selenium									
15. Silver									
16. Sodium									
17. Thallium									
18. Vanadium									
19. Zinc									

COMMENTS: _____

Lab Manager _____

Revision 0
Date September 1986

Form XIII

ICP Linear Ranges

LAB NAME _____ ICP Model Number _____

DATE _____

Analyte	Integration Time (Seconds)	Concentration (ug/L)	Analyte	Integration Time (Seconds)	Concentration (ug/L)
1. Aluminum			13. Magnesium		
2. Antimony			14. Manganese		
3. Arsenic			15. Mercury		
4. Barium			16. Nickel		
5. Beryllium			17. Potassium		
6. Cadmium			18. Selenium		
7. Calcium			19. Silver		
8. Chromium			20. Sodium		
9. Cobalt			21. Thallium		
10. Copper			22. Vanadium		
11. Iron			23. Zinc		
12. Lead					

Footnotes: • Indicate elements not analyzed by ICP with the notation "NA".

COMMENTS: _____

_____

_____

_____

Lab Manager _____

Revision 0
Date September 1986

Organics Analysis Data Sheet
(Page 1)

Sample Number

Laboratory Name: _____ Case No: _____

Lab Sample ID No: _____ QC Report No: _____

Sample Matrix: _____

Data Release Authorized By: _____ Date Sample Received: _____

Volatile Compounds

Date Extracted/Prepared: _____

Date Analyzed: _____

Conc/Dil Factor: _____ pH _____

Percent Moisture: (Not Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
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	
156-60-5	Trans-1, 2-Dichloroethene	
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	

CAS Number		ug/l or ug/Kg (Circle One)
78-87-5	1, 2-Dichloropropane	
10061-02-6	Trans-1, 3-Dichloropropene	
79-01-6	Trichloroethene	
124-48-1	Dibromochloromethane	
79-00-5	1, 1, 2-Trichloroethane	
71-43-2	Benzene	
10061-01-5	cis-1, 3-Dichloropropene	
110-75-8	2-Chloroethylvinylether	
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	
	Total Xylenes	

Data Reporting Qualifiers

For reporting results to EPA, the following results qualifiers are used. Additional flags or footnotes explaining results are encouraged. However, the definition of each flag must be explicit.

Value If the result is a value greater than or equal to the detection limit, report the value

U Indicates compound was analyzed for but not detected. Report the minimum detection limit for the sample with the U (e.g., 10U) based on necessary concentration/dilution action. (This is not necessarily the instrument detection limit.) The footnote should read "U - Compound was analyzed for but not detected. The number is the minimum attainable detection limit for the sample."

J Indicates an estimated value. This flag is used either when estimating a concentration for tentatively identified compounds where a 1:1 response is assumed or when the mass spectral data indicated the presence of a compound that meets the identification criteria but the result is less than the specified detection limit but greater than zero (e.g., 10J). If limit of detection is 10 µg/l and a concentration of 3 µg/l is calculated, report as 3J.

C This flag applies to pesticide parameters where the identification has been confirmed by GC/MS. Single component pesticides ≥ 10 ng/ul in the final extract should be confirmed by GC/MS.

B This flag is used when the analyte is found in the blank as well as a sample. It indicates possible/probable blank contamination and warns the data user to take appropriate action.

Other Other specific flags and footnotes may be required to properly define the results. If used, they must be fully described and such description attached to the data summary report.

Form I

Revision 0
Date September 1986

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 2)

Semivolatile Compounds

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (Decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
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	
39638-32-9	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	Dimethyl Phthalate	
208-96-8	Acenaphthylene	
99-09-2	3-Nitroaniline	

CAS Number		ug/l or ug/Kg (Circle One)
83-32-9	Acenaphthene	
51-28-5	2, 4-Dinitrophenol	
100-02-7	4-Nitrophenol	
132-64-9	Dibenzofuran	
121-14-2	2, 4-Dinitrotoluene	
606-20-2	2, 6-Dinitrotoluene	
84-66-2	Diethylphthalate	
7005-72-3	4-Chlorophenyl-phenylether	
86-73-7	Fluorene	
100-01-6	4-Nitroaniline	
534-52-1	4, 6-Dinitro-2-Methylphenol	
86-30-6	N-Nitrosodiphenylamine (1)	
101-55-3	4-Bromophenyl-phenylether	
118-74-1	Hexachlorobenzene	
87-86-5	Pentachlorophenol	
85-01-8	Phenanthrene	
120-12-7	Anthracene	
84-74-2	Di-n-Butylphthalate	
206-44-0	Fluoranthene	
129-00-0	Pyrene	
85-68-7	Butylbenzylphthalate	
91-94-1	3, 3'-Dichlorobenzidine	
56-55-3	Benzo(a)Anthracene	
117-81-7	bis(2-Ethylhexyl)Phthalate	
218-01-9	Chrysene	
117-84-0	Di-n-Octyl Phthalate	
205-99-2	Benzo(b)Fluoranthene	
207-08-9	Benzo(k)Fluoranthene	
50-32-8	Benzo(a)Pyrene	
193-39-5	Indeno(1, 2, 3-cd)Pyrene	
53-70-3	Dibenz(a, h)Anthracene	
191-24-2	Benzo(g, h, i)Perylene	

(1)-Cannot be separated from diphenylamine

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet
(Page 3)

Pesticide/PCBs

GPC Cleanup ☐Yes ☐No

Date Extracted/Prepared: _____

Separatory Funnel Extraction ☐Yes

Date Analyzed: _____

Continuous Liquid - Liquid Extraction ☐Yes

Conc/Dil Factor: _____

Percent Moisture (decanted) _____

CAS Number		ug/l or ug/Kg (Circle One)
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	
57-74-9	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	

V_i = Volume of extract injected (ul)

V_s = Volume of water extracted (ml)

W_s = Weight of sample extracted (g)

V_t = Volume of total extract (ul)

V_s _____ or W_s _____ V_t _____ V_i _____

Laboratory Name: _____

Case No: _____

Sample Number

Organics Analysis Data Sheet

CAS Number	Compound Name	Fraction	RT or Scan Number	Estimated Concentration (ug/l or ug/kg)
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.				

Form 1, Part B

Revision 0
Date September 1986

WATER SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ **Laboratory Name** _____

	VOLATILE			SEMI-VOLATILE								PESTICIDE
SAMPLE NO.	TOLUENE-D8 (88-110)	BFB (86-115)	1,2 DICHLOROETHANE-D4 (76-114)	NITROBENZENE-D5 (35-114)	2-FLUOROBIPHENYL (43-116)	TERPHENYL-D14 (33-141)			PHENOL-D5 (10-94)	2-FLUOROPHENOL (21-100)	2,4,6 TRIBROMOPHENOL (10-123)	DIBUTYLCHLORENDATE (24-154)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

SOIL SURROGATE PERCENT RECOVERY SUMMARY

Case No. _____ Laboratory Name _____

	VOLATILE			SEMI-VOLATILE							PESTICIDE
SAMPLE NO.	TOLUENE-D8 (81-117)	BFB (74-121)	1,2 DICHLOROETHANE-D4 (70-121)	NITROBENZENE-D5 (23-120)	2-FLUOROBIPHENYL (30-115)	TERPHENYL-D14 (18-137)			PHENOL-D5 (24-113)	2-FLUOROPHENOL (25-121)	2,4,6 TRIBROMOPHENOL (19-122)	DIBUTYLCHLORENDATE (20-150)

VALUES ARE OUTSIDE OF REQUIRED QC LIMITS

Volatiles: _____ out of _____ ; outside of QC limits
Semi-Volatiles: _____ out of _____ ; outside of QC limits
Pesticides: _____ out of _____ ; outside of QC limits

Comments: _____

FORM II

Revision 0
Date September 1986

WATER MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/L)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dichloroethene								14	61-145
	Trichloroethene								14	71-120
SAMPLE NO.	Chlorobenzene								13	75-130
	Toluene								13	76-125
_____	Benzene								11	76-127
B/N	1,2,4-Trichlorobenzene								28	39-98
	Acenaphthene								31	46-118
	2,4 Dinitrotoluene								38	24-96
SAMPLE NO.	Di-n-Butylphthalate								40	11-117
	Pyrene								31	26-127
	N-Nitroso-Di-n-Propylamine								38	41-116
_____	1,4-Dichlorobenzene								28	36-97
ACID	Pentachlorophenol								50	9-103
	Phenol								42	12-89
	2-Chlorophenol								40	27-123
SAMPLE NO.	4-Chloro-3-Methylphenol								42	23-97
_____	4-Nitrophenol								50	10-80
PEST	Lindane								15	56-123
	Heptachlor								20	40-131
	Aldrin								22	40-120
SAMPLE NO.	Dieldrin								18	52-126
	Endrin								21	56-121
_____	4,4'-DDT								27	38-127

ADVISORY LIMITS

RPD: VOAs _____ out of _____; outside QC limits
B/N _____ out of _____; outside QC limits
ACID _____ out of _____; outside QC limits
PEST _____ out of _____; outside QC limits

RECOVERY: VOAs _____ out of _____; outside QC limits
B/N _____ out of _____; outside QC limits
ACID _____ out of _____; outside QC limits
PEST _____ out of _____; outside QC limits

Comments: _____

_____

_____

_____

_____

FORM III

Revision 0
Date September 1986

SOIL MATRIX SPIKE/MATRIX SPIKE DUPLICATE RECOVERY

Case No. _____ **Laboratory Name** _____

FRACTION	COMPOUND	CONC. SPIKE ADDED (ug/Kg)	SAMPLE RESULT	CONC. MS	% REC	CONC. MSD	% REC	RPD	QC LIMITS RPD	QC LIMITS RECOVERY
VOA	1,1-Dicholorethene								22	59-172
	Trichloroethene								24	62-137
SAMPLE NO.	Chlorobenzene								21	60-133
	Toluene								21	59-139
_____	Benzene								21	66-142
B/N	1,2,4-Trichlorobenzene								23	38-107
	Acenaphthene								19	31-137
	2,4 Dinitrotoluene								47	28-89
SAMPLE NO.	Di-n-Butylphthalate								47	29-135
	Pyrene								36	35-142
	N-Nitrosodi-n-Propylamine								38	41-126
_____	1,4-Dichlorobenzene								27	28-104
ACID	Pentachlorophenol								47	17-109
	Phenol								35	26-90
	2-Chlorophenol								50	25-102
SAMPLE NO.	4-Chloro-3-Methylphenol								33	26-103
_____	4-Nitrophenol								50	11-114
PEST	Lindane								50	46-127
	Heptachlor								31	35-130
	Aldrin								43	34-132
SAMPLE NO.	Dieldrin								38	31-134
	Endrin								45	42-139
_____	4,4'-DDT								50	23-134

ADVISORY LIMITS

RPD: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

RECOVERY: VOAs ____ out of ____; outside QC limits
B/N ____ out of ____; outside QC limits
ACID ____ out of ____; outside QC limits
PEST ____ out of ____; outside QC limits

Comments: _____

FORM III

Revision 0
Date September 1986

METHOD BLANK SUMMARY

Case No. _____ Laboratory Name _____

FILE ID	DATE OF ANALYSIS	FRACTION	MATRIX	CONC. LEVEL	INST. ID	CAS NUMBER	COMPOUND (HSL,TIC OR UNKNOWN)	CONC.	UNITS	CRDL

Comments:

GC/MS TUNING AND MASS CALIBRATION
Bromofluorobenzene (BFB)

Case No. _____ **Laboratory Name** _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

m/e	ION ABUNDANCE CRITERIA	%RELATIVE ABUNDANCE
50	15.0 - 40.0% of the base peak	
75	30.0 - 60.0% of the base peak	
95	Base peak, 100% relative abundance	
96	5.0 - 9.0% of the base peak	
173	Less than 1.0% of the base peak	
174	Greater than 50.0% of the base peak	
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]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1]Value in parenthesis is % mass 174.
[2]Value in parenthesis is % mass 176.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

GC/MS TUNING AND MASS CALIBRATION
Decafluorotriphenylphosphine (DFTPP)

Case No. _____ **Laboratory Name** _____

Instrument ID _____ Date _____ Time _____

Data Release Authorized By: _____

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 - 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]

THIS PERFORMANCE TUNE APPLIES TO THE FOLLOWING SAMPLES, BLANKS AND STANDARDS.

[1] Value in parenthesis is % mass 69.
[2] Value in parenthesis is % mass 442.

SAMPLE ID	LAB ID	DATE OF ANALYSIS	TIME OF ANALYSIS

FORM V

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: _____ Instrument I D: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.300 (0.25 for Bromoform)

Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**
Chloromethane								**
Bromomethane								
Vinyl Chloride								*
Chloroethane								
Methylene Chloride								
Acetone								
Carbon Disulfide								
1, 1-Dichloroethene								*
1, 1-Dichloroethane								**
Trans-1, 2-Dichloroethene								
Chloroform								*
1, 2-Dichloroethane								
2-Butanone								
1, 1, 1-Trichloroethane								
Carbon Tetrachloride								
Vinyl Acetate								
Bromodichloromethane								
1, 2-Dichloropropane								*
Trans-1, 3-Dichloropropene								
Trichloroethene								
Dibromochloromethane								
1, 1, 2-Trichloroethane								
Benzene								
cis-1, 3-Dichloropropene								
2-Chloroethylvinylether								
Bromoform								**
4-Methyl-2-Pentanone								
2-Hexanone								
Tetrachloroethene								
1, 1, 2, 2-Tetrachloroethane								**
Toluene								*
Chlorobenzene								**
Ethylbenzene								*
Styrene								
Total Xylenes								

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Volatile HSL Compounds

Case No: ______________ Instrument I D: ______________________

Laboratory Name ______________________ Calibration Date: ______________________

Minimum $\overline{RF}$ for SPCC is **0.300** (0.25 for Bromoform) Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{100}	RF_{150}	RF_{200}	$\overline{RF}$	% RSD	CCC* SPCC**

RF -Response Factor (subscript is the amount of ug/L)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation

CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VI

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	%RSD	CCC* SPCC**
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	†							
Dimethyl Phthalate								
Acenaphthylene								
3-Nitroaniline	†							
Acenaphthene								*
2, 4-Dinitrophenol	†							* *
4-Nitrophenol	†							* *
Dibenzofuran								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)
† -Not detectable at 20 ng

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Instrument ID: _____

Laboratory Name _____ Calibration Date: _____

Minimum $\overline{RF}$ for SPCC is 0.050 Maximum % RSD for CCC is 30%

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC* SPCC**
2, 4-Dinitrotoluene								
2, 6-Dinitrotoluene								
Diethylphthalate								
4-Chlorophenyl-phenylether								
Fluorene								
4-Nitroaniline	†							
4, 6-Dinitro-2-Methylphenol	†							
N-Nitrosodiphenylamine (1)								*
4-Bromophenyl-phenylether								
Hexachlorobenzene								
Pentachlorophenol	†							*
Phenanthrene								
Anthracene								
Di-N-Butylphthalate								
Fluoranthene								*
Pyrene								
Butylbenzylphthalate								
3, 3'-Dichlorobenzidine								
Benzo(a)Anthracene								
bis(2-Ethylhexyl)Phthalate								
Chrysene								
Di-n-Octyl Phthalate								*
Benzo(b)Fluoranthene								
Benzo(k)Fluoranthene								
Benzo(a)Pyrene								*
Indeno(1, 2, 3-cd)Pyrene								
Dibenz(a, h)Anthracene								
Benzo(g, h, i)Perylene								

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† - Not detectable at 20 ng
(1) -Cannot be separated from diphenylamine

Form VI

Revision 0
Date September 1986

Initial Calibration Data
Semivolatile HSL Compounds
(Page 1)

Case No: ____________ Instrument ID: ____________________

Laboratory Name ____________________ Calibration Date: ____________________

Minimum $\overline{RF}$ for SPCC is **0.050** Maximum % RSD for CCC is **30%**

Laboratory ID								
Compound	RF_{20}	RF_{50}	RF_{80}	RF_{120}	RF_{160}	$\overline{RF}$	% RSD	CCC• SPCC••

Response Factor (subscript is the amount of nanograms)
$\overline{RF}$ -Average Response Factor
%RSD -Percent Relative Standard Deviation
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)
† -Not detectable at 20 ng

Form VI

Continuing Calibration Check
Volatile HSL Compounds

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Contract No: _____ **Laboratory ID:** _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.300 (0.25 for Bromoform) Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
Chloromethane					**
Bromomethane					
Vinyl Chloride				*	
Chloroethane					
Methylene Chloride					
Acetone					
Carbon Disulfide					
1, 1-Dichloroethene				*	
1, 1-Dichloroethane					**
Trans-1, 2-Dichloroethene					
Chloroform				*	
1, 2-Dichloroethane					
2-Butanone					
1, 1, 1-Trichloroethane					
Carbon Tetrachloride					
Vinyl Acetate					
Bromodichloromethane					
1, 2-Dichloropropane				*	
Trans-1, 3-Dichloropropene					
Trichloroethene					
Dibromochloromethane					
1, 1, 2-Trichloroethane					
Benzene					
cis-1, 3-Dichloropropene					
2-Chloroethylvinylether					
Bromoform					**
4-Methyl-2-Pentanone					
2-Hexanone					
Tetrachloroethene					
1, 1, 2, 2-Tetrachloroethane					**
Toluene		*		*	
Chlorobenzene					**
Ethylbenzene				*	
Styrene					
Total Xylenes					

RF_{50} -Response Factor from daily standard file at 50 ug/l
RF -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (*)
SPCC -System Performance Check Compounds (**)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Volatile HSL Compounds

Case No: ____________

Laboratory Name ______________________

Contract No: ______________________

Instrument ID: ______________________

Calibration Date: ______________________

Time: ______________________

Laboratory ID: ______________________

Initial Calibration Date: ______________________

Minimum RF for SPCC is 0.300
(0.25 for Bromoform)

Maximum %D for CCC is **25%**

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} -Response Factor from daily standard file at 50 ug l
$\overline{RF}$ -Average Response Factor from initial calibration Form VI

%D -Percent Difference
CCC -Calibration Check Compounds (•)
SPCC -System Performance Check Compounds (••)

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
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 †					
Dimethyl Phthalate					
Acenaphthylene					
3-Nitroaniline †					
Acenaphthene				*	
2, 4-Dinitrophenol †					* *
4-Nitrophenol †					* *
Dibenzofuran					

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

†-Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (*)

SPCC -System Performance Check Compounds (**)

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 2)

Case No: _____ Calibration Date: _____

Laboratory Name _____ Time: _____

Laboratory ID: _____

Instrument ID: _____ Initial Calibration Date: _____

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC
2, 4-Dinitrotoluene					
2, 6-Dinitrotoluene					
Diethylphthalate					
4-Chlorophenyl-phenylether					
Fluorene					
4-Nitroaniline †					
4, 6-Dinitro-2-Methylphenol †					
N-Nitrosodiphenylamine (1)				*	
4-Bromophenyl-phenylether					
Hexachlorobenzene					
Pentachlorophenol †				*	
Phenanthrene					
Anthracene					
Di-N-Butylphthalate					
Fluoranthene				*	
Pyrene					
Butylbenzylphthalate					
3, 3'-Dichlorobenzidine					
Benzo(a)Anthracene					
bis(2-Ethylhexyl)Phthalate					
Chrysene					
Di-n-Octyl Phthalate				*	
Benzo(b)Fluoranthene					
Benzo(k)Fluoranthene					
Benzo(a)Pyrene				*	
Indeno(1, 2, 3-cd)Pyrene					
Dibenz(a, h)Anthracene					
Benzo(g, h, i)Perylene					

RF_{50} - Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ - Average Response Factor from initial calibration Form VI

%D - Percent Difference

† - Due to low response, analyze at 80 total nanograms

CCC - Calibration Check Compounds (*)

SPCC - System Performance Check Compounds (**)

(1) - Cannot be separated from diphenylamine

Form VII

Revision 0
Date September 1986

Continuing Calibration Check
Semivolatile HSL Compounds
(Page 1)

Case No: ______________ Calibration Date: ______________

Laboratory Name ______________ Time: ______________

Laboratory ID: ______________

Instrument ID: ______________ Initial Calibration Date: ______________

Minimum RF for SPCC is 0.050 Maximum %D for CCC is 25%

Compound	$\overline{RF}$	RF_{50}	% D	CCC	SPCC

RF_{50} -Response Factor from daily standard file at concentration indicated (50 total nanograms)

$\overline{RF}$ -Average Response Factor from initial calibration Form VI

† -Due to low response, analyze at 80 total nanograms

%D -Percent Difference

CCC -Calibration Check Compounds (·)

SPCC System Performance Check Compounds (··)

Form VII

Pesticide Evaluation Standards Summary
(Page 1)

Case No: _____ **Laboratory Name**: _____

GC Column: _____

Date of Analysis: _____ Instrument ID: _____

Evaluation Check for Linearity

Laboratory ID				
Pesticide	Calibration Factor Eval. Mix A	Calibration Factor Eval. Mix B	Calibration Factor Eval. Mix C	% RSD (≤10%)
Aldrin				
Endrin				
4,4'- DDT(1)				
Dibutyl Chlorendate				

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

	Laboratory I.D.	Time of Analysis	Endrin	4,4'- DDT	Combined(2)
Eval Mix B 72 Hour					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					
Eval Mix B					

(1) See Exhibit E, Section 7.5.4
(2) See Exhibit E, Section 7.3.1.2.2.1

Pesticide Evaluation Standards Summary
(Page 2)

Evaluation of Retention Time Shift for Dibutyl Chlorendate

Report all standards, blanks and samples

Sample No	Lab I.D.	Time of Analysis	Percent Diff.	SMO Sample No.	Lab I.D.	Time of Analysis	Percent Diff.

Form VIII (Continued)

RCRA
4/86

PESTICIDE/PCB STANDARDS SUMMARY

Case No. _____ Laboratory Name _____

GC Column _____ GC Instrument ID _____

	DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____				DATE OF ANALYSIS _____ TIME OF ANALYSIS _____ LABORATORY ID _____			
COMPOUND	RT	RETENTION TIME WINDOW	CALIBRATION FACTOR	CONF. OR QUANT.	RT	CALIBRATION FACTOR	CONF. OR QUANT.	PERCENT DIFF.**
alpha-BHC								
beta-BHC								
delta-BHC								
gamma-BHC								
Heptachlor								
Aldrin								
Heptachlor Epoxide								
Endosulfan I								
Dieldrin								
4,4'-DDE								
Endrin								
Endosulfan II								
4,4'-DDD								
Endrin Aldehyde								
Endosulfan Sulfate								
4,4'-DDT								
Methoxychlor								
Endrin Ketone								
Tech. Chlordane								
alpha-Chlordane								
gamma-Chlordane								
Toxaphene								
Aroclor - 1016								
Aroclor - 1221								
Aroclor - 1232								
Aroclor - 124.								
Aroclor - 1248								
Aroclor - 1254								
Aroclor - 1260								

** CONF. = CONFIRMATION (<20% DIFFERENCE)
QUANT. = QUANTITATION (<15% DIFFERENCE)

FORM IX

Revision 0
Date September 1986

Pesticide/PCB Identification

Case No. ______________________ **Laboratory Name** ______________________

SAMPLE ID	PRIMARY COLUMN	PESTICIDE/ PCB	RT OF TENTATIVE ID	RT WINDOW OF APPROPRIATE STANDARD	CONFIRMATION COLUMN	RT ON CONFIRMATORY COLUMN	RT WINDOW OF APPROPRIATE STANDARD	GC/MS CONFIRMED (Y or N)

FORM X

CHAPTER FOUR

ORGANIC ANALYTES

4.1 SAMPLING 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.

4.1.2 Sample Handling and Preservation

This section deals separately with volatile and semivolatile organics. Refer to Chapter Two (Table 2-16) and Table 4-1 of this Section for recommended sample containers, sample preservation, and sample holding times.

Volatile Organics

Standard 40-mL glass screw-cap VOA vials with Teflon-faced silicone septum may be used for both liquid and solid matrices. The vials and septum should be soap and water washed and rinsed with distilled deionized water. After thoroughly cleaning the vials and septum, they should be placed in a muffle furnace and dried at 105°C for approximately one hour. (Note: Do not heat the septum for extended periods of time, i.e., more than one hr, 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. 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. Each VOA vial should be filled until there is a meniscus over the lip of the vial. The screw-top lid with the septum (Teflon side toward the sample) should then be tightened onto the vial. After tightening the lid, the vial should be inverted and tapped to check for air bubbles. If there are any air bubbles present the sample must be retaken. Two VOA vials should be filled per sample location.

VOA vials for samples with solid or semi-solid (sludges) matrices 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.

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 locations 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 distilled deionized water should be carried throughout the sampling, storage, and shipping process.

Semivolatile Organics (This includes Pesticides 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-top covers with Teflon liners. In situations where Teflon is not available, solvent-rinsed aluminum foil may be used as a liner. Highly 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 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 lesser volume. The process of concentrating the compounds of interest in this operation may similarly concentrate the contamination substance, 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 flotate most particulate material;

3. Hot-water rinse to flush away flotated 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. 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 will be discussed in the order in which they appear above.

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 methanol-flushed before it is placed in the hot detergent soak. If this is not done, the soak bath may serve to contaminate <u>all other</u> 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 H_2SO_4 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 because contaminants can be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles such as stirring rods, glass stoppers, and bottle caps can be wrapped in aluminum foil and oven-dried a short time if oven space is available. 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 alternative to air drying, the glassware can be heated to a minimum of 300°C to vaporize any organics.

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

Parameter	Container	Preservative	Holding Time
Volatile Organics			
Concentrated Waste Samples	8-oz. widemouth glass with Teflon liner	None	14 days
Liquid Samples			
No Residual Chlorine Present	2 40-mL vials with Teflon lined septum caps	4 drops conc. HCl, Cool, 4°C	14 days
Residual Chlorine Present	2 40-mL vials with Teflon lined septum caps	Collect sample in a 4 oz. soil VOA container which has been pre-preserved with 4 drops of 10% sodium thiosulfate. Gently mix sample and transfer to a 40-mL VOA vial that has been pre-preserved with 4 drops conc. HCl, Cool to 4°C	14 days
Acrolein and Acrylonitrile	2 40-mL vials with Teflon lined septum caps	Adjust to pH 4-5, Cool, 4°C	14 days
Soil/Sediments and Sludges	4-oz (120-mL) widemouth glass with Teflon liner	Cool, 4°C	14 days

TABLE 4-1. Continued

Parameter	Container	Preservative	Holding Time
Semivolatile Organics			
Concentrated Waste Samples	8-oz. widemouth glass with Teflon liner	None	14 days
Liquid Samples			
No Residual Chlorine Present	1-gal. or 2 1/2-gal. amber glass with Teflon liner	Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days
Residual Chlorine Present	1-gal. or 2 1/2-gal. amber glass with Teflon liner	Add 3 mL 10% sodium thiosulfate per gallon, Cool, 4°C	Samples must be extracted within 7 days and extracts analyzed within 40 days
Soil/Sediments and Sludges	8-oz. widemouth glass with Teflon liner	Cool, 4°C	14 days

4.2 SAMPLE PREPARATION METHODS

4.2.1 EXTRACTIONS AND PREPARATIONS

METHOD 3500

ORGANIC EXTRACTION AND SAMPLE PREPARATION

1.0 SCOPE AND APPLICATION

1.1 The 3500 Methods are procedures for quantitatively extracting nonvolatile and semivolatile organic compounds from various sample matrices. Cleanup and/or analysis of the resultant extracts are described in Chapter Four, Sections 4.2.2 and 4.3, respectively.

1.2 Method 3580 describes a solvent dilution technique that may be used on non-aqueous nonvolatile and semivolatile organic samples prior to cleanup and/or analysis.

1.3 The 5000 Methods are procedures for preparing samples containing volatile organic compounds for quantitative analysis.

1.4 Refer to the specific method of interest for further details.

2.0 SUMMARY OF METHOD

2.1 3500 Methods: A sample of a known volume or weight is solvent extracted. The resultant extract is dried and then concentrated in a Kuderna-Danish apparatus. Other concentration devices or techniques may be used in place of the Kuderna-Danish concentrator if the quality control requirements of the determinative methods are met (Method 8000, Section 8.0).

2.2 5000 Methods: Refer to the specific method of interest.

3.0 INTERFERENCES

3.1 Samples requiring analysis for volatile organic compounds, 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 reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.2 Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required. Refer to Chapter One for specific guidance on quality control procedures.

3.3 Interferences coextracted from the samples will vary considerably from source to source. If analysis of an extracted sample is prevented due to interferences, further cleanup of the sample extract may be necessary. Refer to Method 3600 for guidance on cleanup procedures.

3.4 Phthalate esters contaminate many types of products commonly found in the laboratory. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.5 Glassware contamination resulting in analyte degradation: Soap residue on glassware may cause degradation of certain analytes. Specifically, aldrin, heptachlor, and most organophosphorous pesticides will degrade in this situation. This problem is especially pronounced with glassware that may be difficult to rinse (e.g., 500-mL K-D flask). These items should be hand-rinsed very carefully to avoid this problem.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific method of interest for a description of the apparatus and materials needed.

5.0 REAGENTS

5.1 Refer to the specific method of interest for a description of the solvents needed.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions.

5.2.1 **Purgeable stock standards:** 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.

5.2.1.1 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 0.1 mg.

5.2.1.2 Using a 100-uL 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.

5.2.1.3 Reweigh, dilute to volume, stopper, then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

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

5.2.1.5 All standards must be replaced after 1 month, or sooner if comparison with check standards indicates a problem.

5.2.2 **Semivolatile stock standards:** Base/neutral and acid stock standards are prepared in methanol. Organochlorine pesticide standards are prepared in acetone.

5.2.2.1 Stock standard solutions should be stored in Teflon-sealed containers at 4°C. The solutions should be checked frequently for stability. These solutions must be replaced after six months, or sooner if comparison with quality control check samples indicate a problem.

5.3 Surrogate standards: A surrogate standard (i.e., a chemically inert compound not expected to occur in an environmental sample) should be added to each sample, blank, and matrix spike sample just prior to extraction or processing. The recovery of the surrogate standard is used to monitor for unusual matrix effects, gross sample processing errors, etc. Surrogate recovery is evaluated for acceptance by determining whether the measured concentration falls within the acceptance limits. Recommended surrogates for different analyte groups follow; however, these compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well. Normally three or more standards are added for each analyte group.

5.3.1 **Base/neutral and acid surrogate spiking solutions:** The following are recommended surrogate standards.

Base/neutral	Acid
2-Fluorobiphenyl	2-Fluorophenol
Nitrobenzene-d_5	2,4,6-Tribromophenol
Terphenyl-d_{14}	Phenol-d_6

5.3.1.1 Prepare a surrogate standard spiking solution in methanol that contains the base/neutral compounds at a concentration of 100 ug/mL, and the acid compounds at 200 ug/mL for water and sediment/soil samples (low- and medium-level). For waste samples, the concentration should be 500 ug/mL for base/neutrals and 1000 ug/mL for acids.

5.3.2 **Organochlorine pesticide surrogate spiking solution:** The following are recommended surrogate standards for organochlorine pesticides.

Organochlorine pesticides

Dibutylchlorendate (DBC)
2,4,5,6-Tetrachloro-meta-xylene (TCMX)

5.3.2.1 Prepare a surrogate standard spiking solution at a concentration of 1 ug/mL in acetone for water and sediment/soil samples. For waste samples, the concentration should be 5 ug/mL.

5.3.3 **Purgeable surrogate spiking solution:** The following are recommended surrogate standards for volatile organics.

Purgeable organics

p-Bromofluorobenzene
1,2-Dichloroethane-d_4
Toluene-d_8

5.3.3.1 Prepare a surrogate spiking solution (as described in Paragraph 5.2.1 or through secondary dilution of the stock standard) in methanol containing the surrogate standards at a concentration of 25 ug/mL.

5.4 Matrix spike standards: Select five or more analytes from each analyte group for use in a spiking solution. The following are recommended matrix spike standard mixtures for a few analyte groups. These compounds, or others that better correspond to the analyte group, may be used for other analyte groups as well.

5.4.1 **Base/neutral and acid matrix spiking solution:** Prepare a spiking solution in methanol that contains each of the following base/neutral compounds at 100 ug/mL and the acid compounds at 200 ug/mL for water and sediment/soil samples. The concentration of these compounds should be five times higher for waste samples.

Base/neutrals	Acids
1,2,4-Trichlorobenzene	Pentachlorophenol
Acenaphthene	Phenol
2,4-Dinitrotoluene	2-Chlorophenol
Pyrene	4-Chloro-3-methylphenol
N-Nitroso-di-n-propylamine	4-Nitrophenol
1,4-Dichlorobenzene	

5.4.2 **Organochlorine pesticide matrix spiking solution:** Prepare a spiking solution in acetone or methanol that contains the following pesticides in the concentrations specified for water and sediment/soil. The concentration should be five times higher for waste samples.

Pesticide	Concentration (ug/mL)
Lindane	0.2
Heptachlor	0.2
Aldrin	0.2
Dieldrin	0.5
Endrin	0.5
4,4'-DDT	0.5

5.4.3 **Purgeable matrix spiking solution:** Prepare a spiking solution in methanol that contains the following compounds at a concentration of 25 ug/mL.

Purgeable organics

1,1-Dichloroethene
Trichloroethene
Chlorobenzene
Toluene
Benzene

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material to the Organic Analyte Chapter, Section 4.1.

7.0 PROCEDURE

7.1 Semivolatile organic sample extraction: Water, soil/sediment, sludge, and waste samples requiring analysis for base/neutral and acid extractables and/or organochlorine pesticides must undergo solvent extraction prior to analysis. This manual contains four methods that may be used for this purpose: Method 3510; Method 3520; Method 3540; and Method 3550. The method that should be used on a particular sample, is highly dependent upon the physical characteristics of that sample. Therefore, review these four methods prior to choosing one in particular. Appropriate surrogate standards and, if necessary, matrix spiking solutions are added to the sample prior to extraction for all four methods.

7.1.1 **Method 3510:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is solvent extracted using a separatory funnel. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. Method 3520 should be used if an emulsion forms between the solvent-sample phases, which can not be broken up by mechanical techniques.

7.1.2 **Method 3520:** Applicable to the extraction and concentration of water-insoluble and slightly water-soluble organics from aqueous samples. A measured volume of sample is extracted with an organic solvent in a continuous liquid-liquid extractor. The solvent must have a density greater than that of the sample. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis. The limitations of Method 3510 concerning solvent-sample phase separation do not interfere with this procedure.

7.1.3 **Method 3540:** This is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. A solid sample is mixed with anhydrous sodium sulfate, placed into an extraction thimble or between two plugs of glass wool, and extracted using an appropriate solvent in a Soxhlet extractor. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.4 **Method 3550:** This method is applicable to the extraction of nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes using the technique of sonication. Two procedures are detailed depending upon the expected concentration of organics in the sample; a low concentration and a high concentration method. In both, a known weight of sample is mixed with anhydrous sodium sulfate and solvent extracted using sonication. The extract is dried, concentrated and, if necessary, exchanged into a solvent compatible with further analysis.

7.1.5 **Method 3580:** This method describes the technique of solvent dilution of non-aqueous waste samples. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

7.2 Volatile organic sample preparation: There are three methods for volatile sample preparation: Method 5030; Method 5040; and direct injection. Method 5030 is the most widely applicable procedure for analysis of volatile organics, while the direct injection technique may have limited applicability to aqueous matrices.

7.2.1 **Method 5030:** This method describes the technique of purge-and-trap for the introduction of purgeable organics into a gas chromatograph. This procedure is applicable for use with aqueous samples directly and to solids, wastes, soils/sediments, and water-miscible liquids following appropriate preparation. An inert gas is bubbled through the sample, which will efficiently transfer the purgeable organics from the aqueous phase to the vapor phase. The vapor phase is swept through a sorbent trap where the purgeables are trapped. After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. Prior to application of the purge-and-trap procedure, all samples (including blanks, spikes, and duplicates) should be spiked with surrogate standards and, if required, with matrix spiking compounds.

7.2.2 **Method 5040:** This method is applicable to the investigation of sorbent cartridges from volatile organic sampling train (VOST).

7.3 Sample analysis: Following preparation of a sample by one of the methods described above, the sample is ready for further analysis. For samples requiring volatile organic analysis, application of one of the three methods described above is followed directly by gas chromatographic analysis (Methods 8010, 8015, 8020, or 8030). Samples prepared for semivolatile analysis may, if necessary, undergo cleanup (See Method 3600) prior to application of a specific determinative method.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific guidance on quality control procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples are processed, a method blank(s) should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Surrogate standards should be added to all samples when specified in the appropriate determinative method in Chapter Four, Section 4.3.

8.4 A reagent blank, a matrix spike, and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

8.5 For GC or GC/MS analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. Method 8000, Section 8.0 discusses in detail the process of verification; however, preparation of the QC check sample concentrate is dependent upon the method being evaluated.

8.5.1 **Volatile organic QC check samples:** QC check sample concentrates containing each analyte of interest are spiked into reagent water (defined as the QC check sample) and analyzed by purge-and-trap (Method 5030). The concentration of each analyte in the QC check sample is 20 ug/L. The evaluation of system performance is discussed in detail in Method 8000, beginning with Paragraph 8.6.

8.5.2 **Semivolatile organic QC check samples:** To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1-L aliquots of reagent water (now called the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the manual. Method 8000 discusses in detail the procedure of verifying the detection system once the QC check sample has been prepared. The concentrations of the QC check sample concentrate for the various methods are as follows:

8.5.2.1 Method 8040 - Phenols: The QC check sample concentrate should contain each analyte at a concentration of 100 ug/mL in 2-propanol.

8.5.2.2 Method 8060 - Phthalate esters: The QC check sample concentrate should contain the following analytes at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl)phthalate, 50 ug/mL; di-n-octylphthalate, 50 ug/mL; and any other phthalate at 25 ug/mL.

8.5.2.3 Method 8080 - Organochlorine pesticides and PCBs: The QC check sample concentrate should contain each single-component analyte at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; and any other single-component pesticide at 2 ug/mL. If the method is only to be used to analyze PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multicomponent parameter at a concentration of 50 ug/mL in acetone.

8.5.2.4 Method 8090 - Nitroaromatics and Cyclic Ketones: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: each dinitrotoluene at 20 ug/mL; and isophorone and nitrobenzene at 100 ug/mL.

8.5.2.5 Method 8100 - Polynuclear aromatic hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene 5 ug/mL; and any other PAH at 10 ug/mL.

8.5.2.6 Method 8120 - Chlorinated hydrocarbons: The QC check sample concentrate should contain each analyte at the following concentrations in acetone: hexachloro-substituted hydrocarbons, 10 ug/mL; and any other chlorinated hydrocarbon, 100 ug/mL.

9.0 METHOD PERFORMANCE

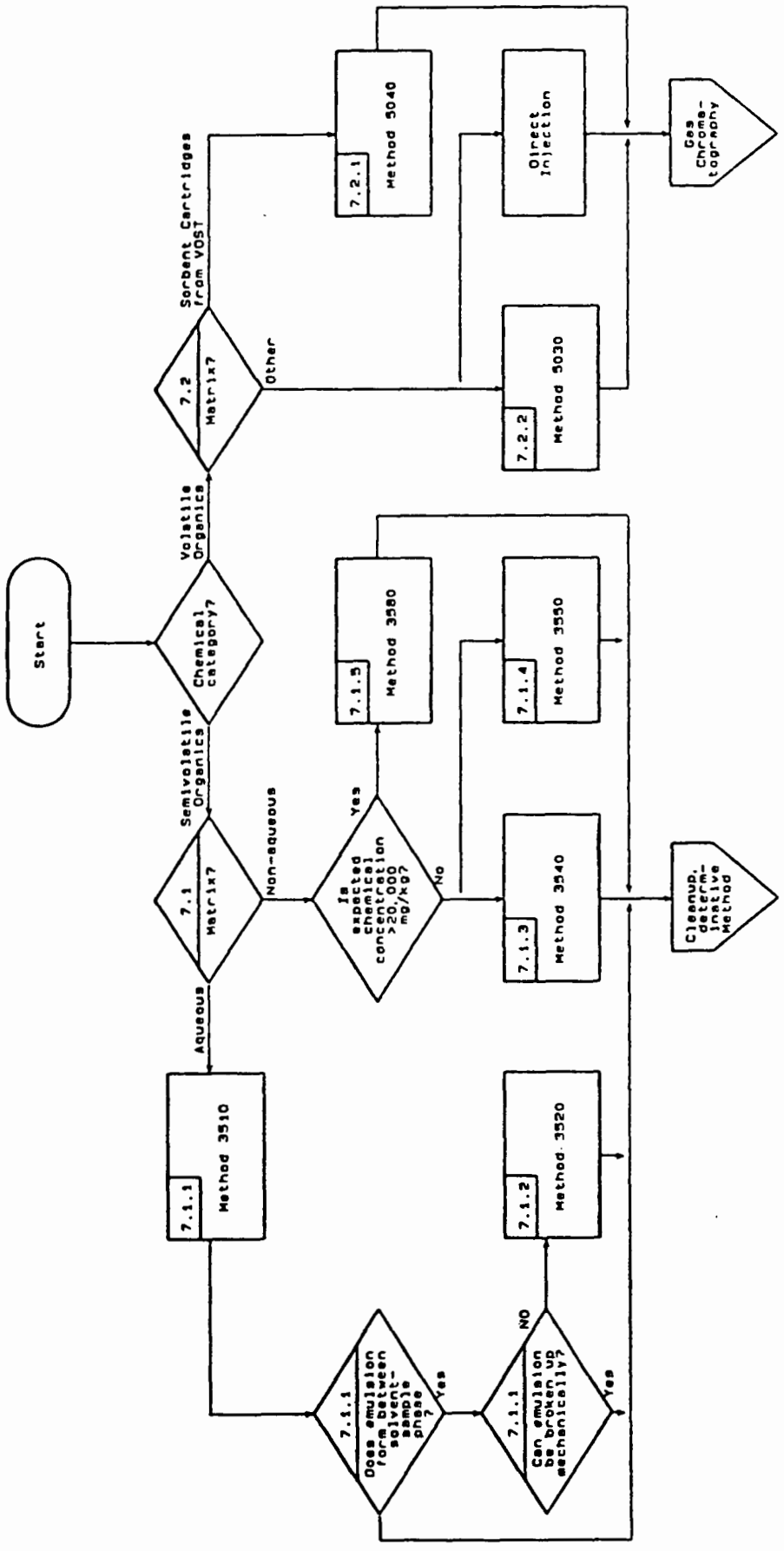
9.1 The recovery of surrogate standards is used to monitor unusual matrix effects, sample processing problems, etc. The recovery of matrix spiking compounds indicates the presence or absence of unusual matrix effects.

9.2 The performance of this method will be dictated by the overall performance of the sample preparation in combination with the analytical determinative method.

10.0 REFERENCES

10.1 None required.

METHOD 3500
ORGANIC EXTRACTION AND SAMPLE PREPARATION



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 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, 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.

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

[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.

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 (±5°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 water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution, 10 N: (ACS) Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

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

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 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, Section 4.1.

7.0 PROCEDURE

7.1 Using a 1-liter graduated cylinder, measure 1 liter of sample and transfer it to the separatory funnel. 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 min 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 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample 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 Paragraphs 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 Synder 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 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 from the water bath and allow it to drain and cool for at least 10 min.

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 re-attach the Snyder column. Concentrate the extract, as described in Paragraph 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 Paragraph 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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Synder 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 Paragraph 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 Teflon-sealed screw-cap vial 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

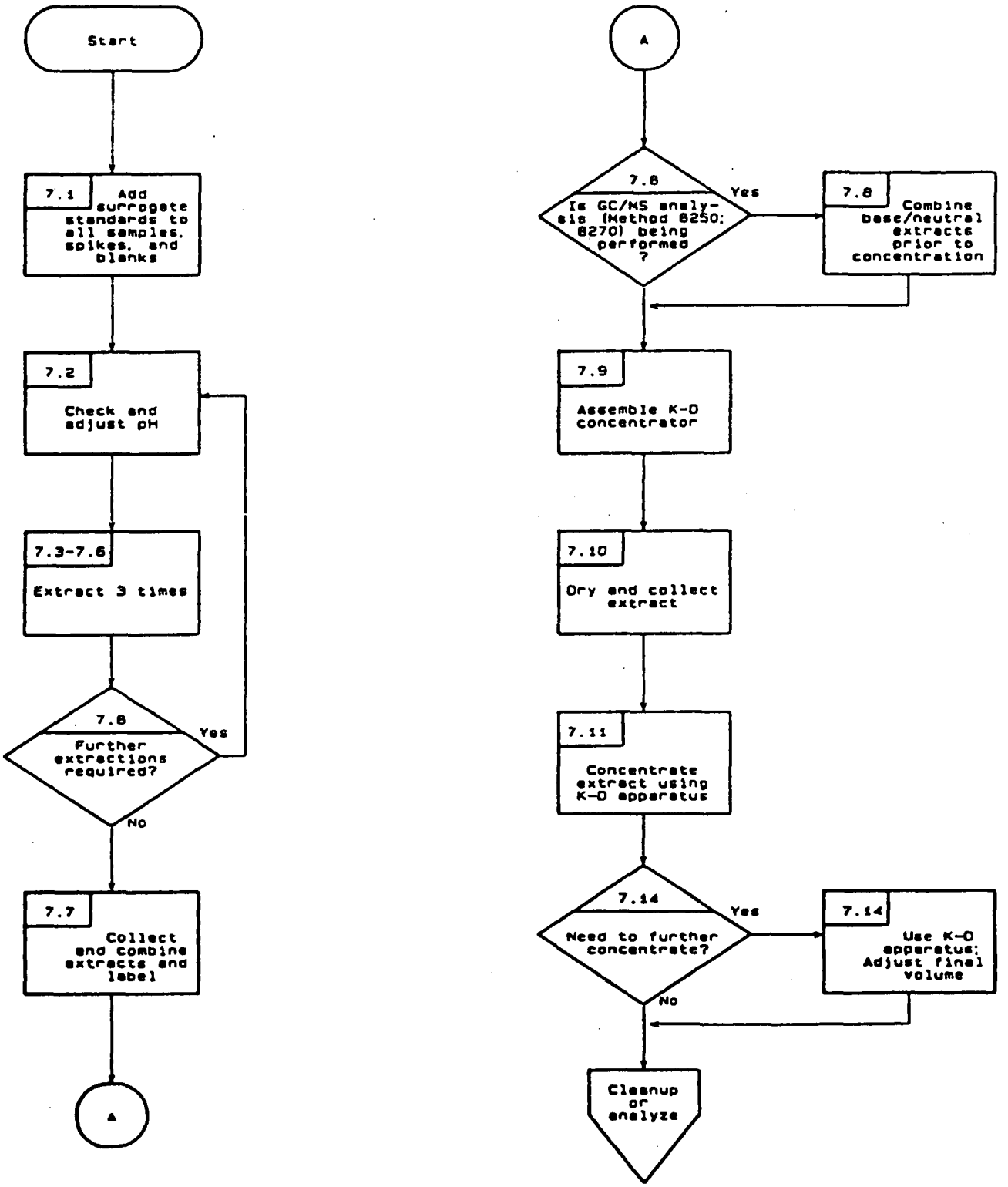
9.1 Refer to the determinative methods for performance data.

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.

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 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 hr. 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.

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[b]	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

[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.

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 (±5°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 Heating mantle: Rheostat controlled.

4.9 Syringe: 5-mL.

4.10 Graduated cylinder: 1-liter.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution, 10 N: (ACS) Dissolve 40 g NaOH in reagent water and dilute to 100 mL.

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

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL of H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 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, Section 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. 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 reagent water to the extractor to ensure proper operation and extract for 18-24 hr.

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 Section 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 hr, 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 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 from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower 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 re-attach the Snyder column. Concentrate the extract, as described in Paragraph 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 Paragraph 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 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Synder 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 1.0-2.0 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 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 Teflon-sealed screw-cap vial 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

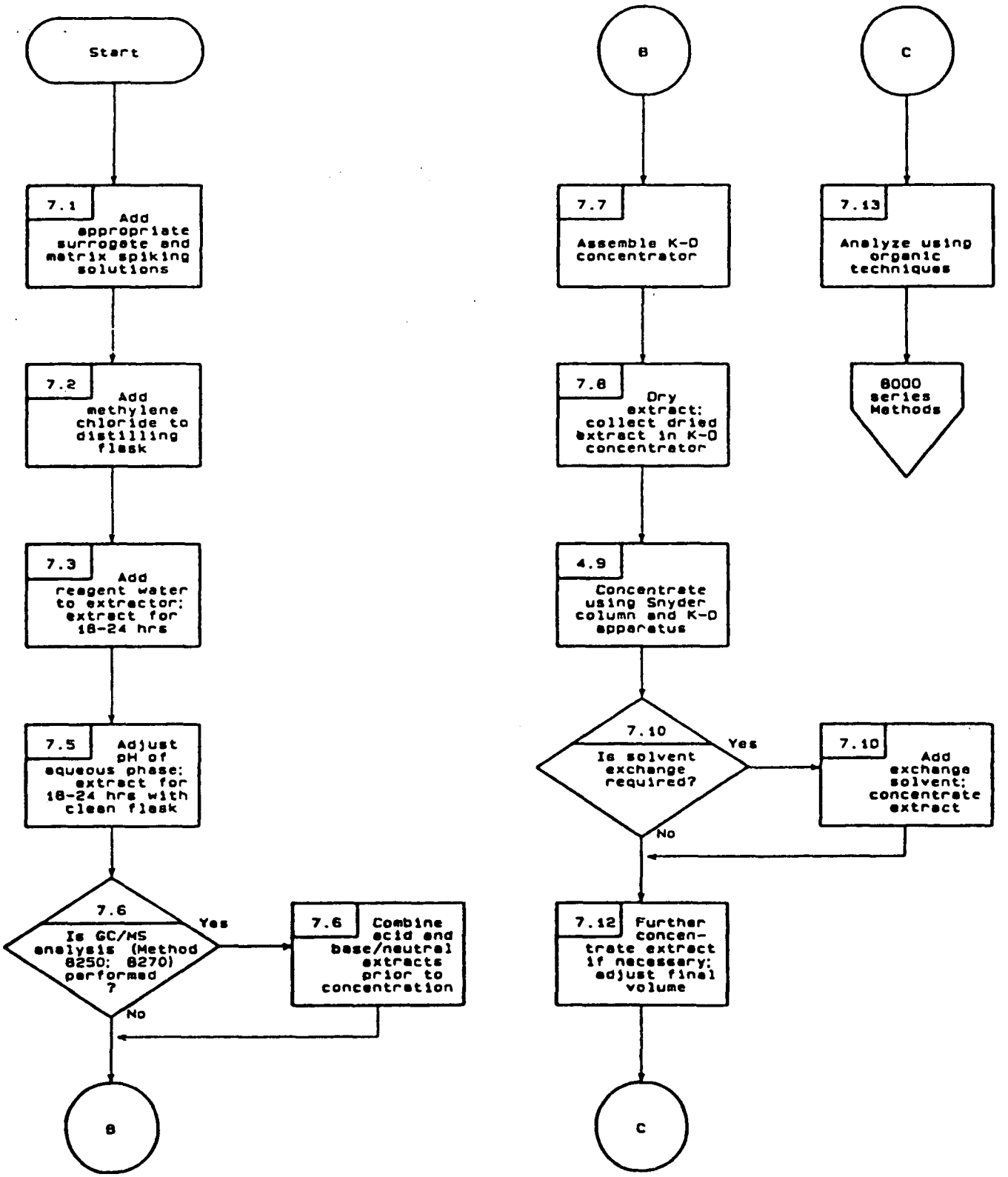
9.1 Refer to the determinative methods for performance data.

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.

METHOD 3520

CONTINUOUS LIQUID-LIQUID EXTRACTION



Revision 0
Date September 1986

METHOD 3540

SOXHLET EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3540 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, 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 (±5°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 water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium sulfate: (ACS) Granular anhydrous (purified by washing with methylene chloride followed by heating at 400°C for 4 hr in a shallow tray).

5.3 Extraction solvents:

5.3.1 Soil/sediment and aqueous sludge samples shall be extracted using either of the following solvent systems.

5.3.1.1 Toluene/Methanol: 10:1 (v/v), pesticide quality or equivalent.

5.3.1.2 Acetone/Hexane: 1:1 (v/v), pesticide quality or equivalent.

5.3.2 Other samples shall be extracted using the following:

5.3.2.1 Methylene chloride: pesticide quality or equivalent.

5.4 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, 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.

7.2 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:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

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 (Section 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 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 100-125 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 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 from the water bath and allow it to drain and cool for at least 10 min.

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 re-attach the Snyder column. Concentrate the extract as described in Paragraph 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 Paragraph 7.9 or adjusted to 10.0 mL with the solvent last used.

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.

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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower 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 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 Teflon-sealed screw-cap vial 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

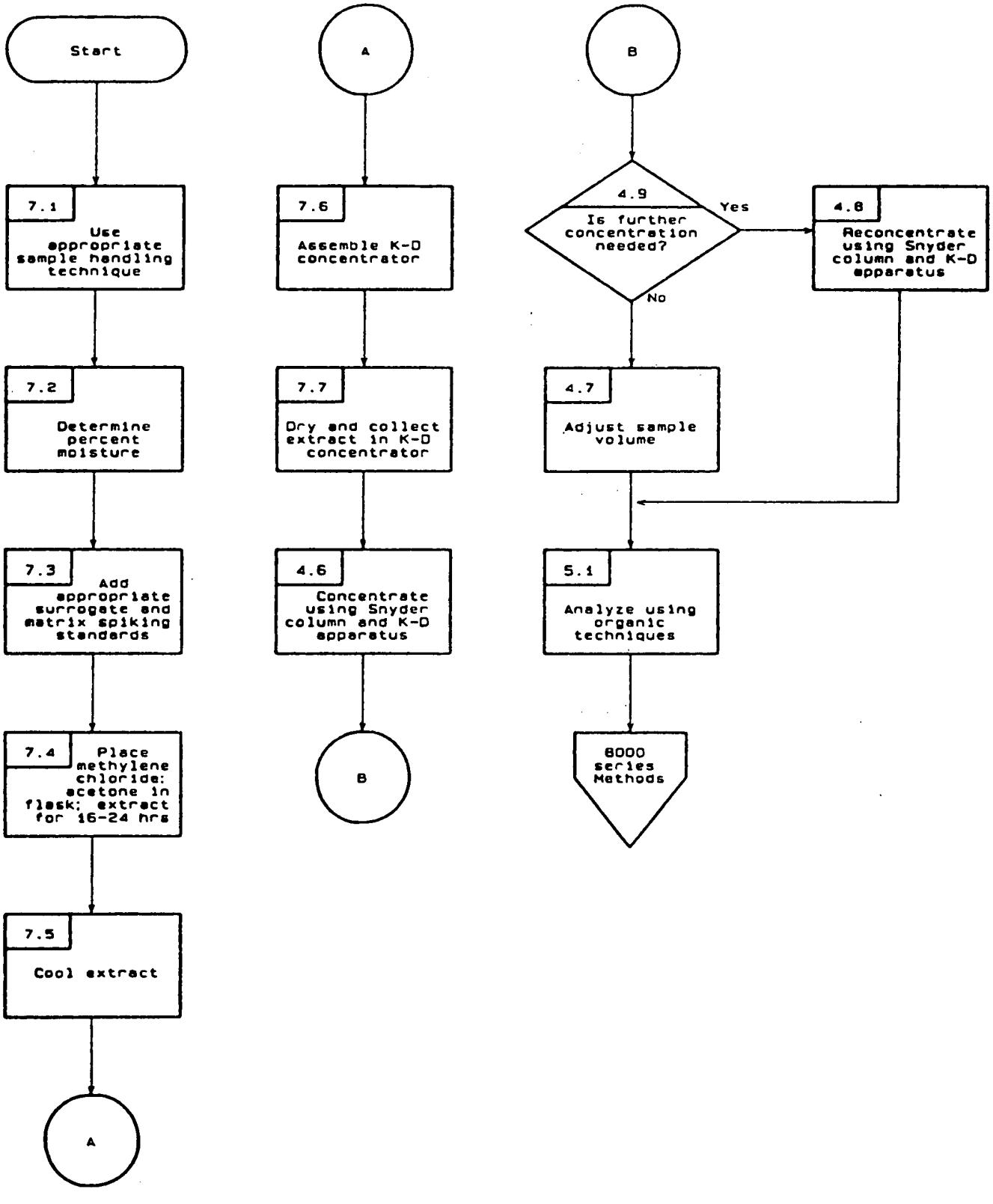
9.1 Refer to the determinative methods for performance data.

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.

METHOD 3540

SOXHLET EXTRACTION



Revision 0
Date September 1986

METHOD 3550

SONICATION EXTRACTION

1.0 SCOPE AND APPLICATION

1.1 Method 3550 is a procedure for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The sonication 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 $\leq$20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The 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 Cleanup, Section 4.2.2 of Chapter Four, 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 sonication. The extract is separated from the sample by vacuum filtration or centrifugation. The extract is ready for cleanup and/or analysis following concentration.

2.2 High concentration method: A 2-g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This is solvent extracted once using sonication. A portion of the extract is removed for cleanup and/or analysis.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Apparatus for grinding: If the sample will not pass through a 1-mm standard sieve or cannot be extruded through a 1-mm opening, it should be processed into a homogeneous sample that meets these requirements. Fisher Mortar Model 155 Grinder, Fisher Scientific Co., Catalogue Number 8-323, or an equivalent brand and model, is recommended for sample processing. This grinder should handle most solid samples, except gummy, fibrous, or oily materials.

4.2 Sonication: A horn-type sonicator equipped with a titanium tip should be used. The following sonicator, or an equivalent brand and model, is recommended:

Ultrasonic cell disrupter: Heat Systems - Ultrasonics, Inc., Model W-385 (475 watt) sonicator or equivalent (Power wattage must be a minimum of 375 with pulsing capability and No. 200 1/2" Tapped Disrupter Horn) plus No. 207 3/4" Tapped Disrupter Horn, and No. 419 1/8" Standard Tapered microtip probe.

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 moisture:

4.4.1 **Oven:** Drying.

4.4.2 **Desiccator.**

4.4.3 **Crucibles:** Porcelain.

4.5 Pasteur glass pipets: Disposable, 1-mL.

4.6 Beakers: 400-mL.

4.7 Vacuum 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).

4.8.2 **Evaporator flask:** 500-mL (Kontes K-570001-0500 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).

4.9 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 (±5°C). The bath should be used in a hood.

4.11 Balance: Top-loading, capable of accurately weighing 0.01 g.

4.12 Vials and caps: 2-mL for GC auto-sampler.

4.13 Glass scintillation vials: At least 20-mL, with screw-cap and Teflon or aluminum foil liner.

4.14 Spatula: Stainless steel or Teflon.

4.15 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.

4.16 Syringe: 5-mL.

5.0 REAGENTS

5.1 Sodium sulfate: Anhydrous and reagent grade, heated at 400°C for 4 hr, cooled in a desiccator, and stored in a glass bottle. Baker anhydrous powder, catalog #73898, or equivalent.

5.2 Extraction solvents: Methylene chloride:acetone (1:1, v:v), methylene chloride, hexane (pesticide quality or equivalent).

5.3 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, 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.

7.2 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:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3 Determination of pH (if required): Transfer 50 g of sample to a 100-mL beaker. Add 50 mL of water and stir for 1 hr. Determine the pH of sample with glass electrode and pH meter while stirring. Discard this portion of sample.

7.4 Extraction method for samples expected to contain low concentrations of organics and pesticides ($\lesssim$20 mg/kg):

7.4.1 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 weight to the nearest 0.1 g. Non-porous 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. The sample should be free-flowing at this point. Add 1 mL of 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 of the extract is lost due to loading of the GPC column. Immediately add 100 mL of 1:1 methylene chloride:acetone.

7.4.2 Place the bottom surface of the tip of the #207 3/4 in. disruptor horn about 1/2 in. below the surface of the solvent, but above the sediment layer.

7.4.3 Sonicate for 3 min, with output control knob set at 10 and with mode switch on Pulse and percent-duty cycle knob set at 50%. Do NOT use microtip probe.

7.4.4 Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge and decant extraction solvent.

7.4.5 Repeat the extraction two or more times with two additional 100-mL portions of solvent. Decant off the extraction solvent after each sonication. On the final sonication, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

7.4.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask.

7.4.7 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 100-125 mL of extraction solvent to complete the quantitative transfer.

7.4.8 Add one or two clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL 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.

7.4.9 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 re-attach the Snyder column. Concentrate the extract as described in Paragraph 7.4.8, raising the temperature of the water bath, if necessary, to maintain proper distillation.

7.4.10 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 Paragraph 7.4.11 or adjusted to 10.0 mL with the solvent last used.

7.4.11 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 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the liquid

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.

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 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with approximately 0.2 mL of appropriate solvent. Adjust the final volume to the volume required for cleanup or for the determinative method (see Table 1).

7.4.12 Transfer the concentrated extract to a clean screw-cap vial. Seal the vial with a Teflon-lined lid and mark the level on the vial. Label with the sample number and fraction and store in the dark at 4°C until ready for analysis or cleanup.

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/uL of each base/neutral analyte and 400 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.

7.5.4 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 min at output control setting 5 and with mode switch on pulse and percent duty cycle of 50%. Extraction solvents are:

1. Nonpolar compounds, i.e., organochlorine pesticides and PCBs: hexane.

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 Paragraphs 7.4.6 through 7.4.12 for details on concentration. Normally, the 5.0 mL extract is concentrated to 1.0 mL.

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.

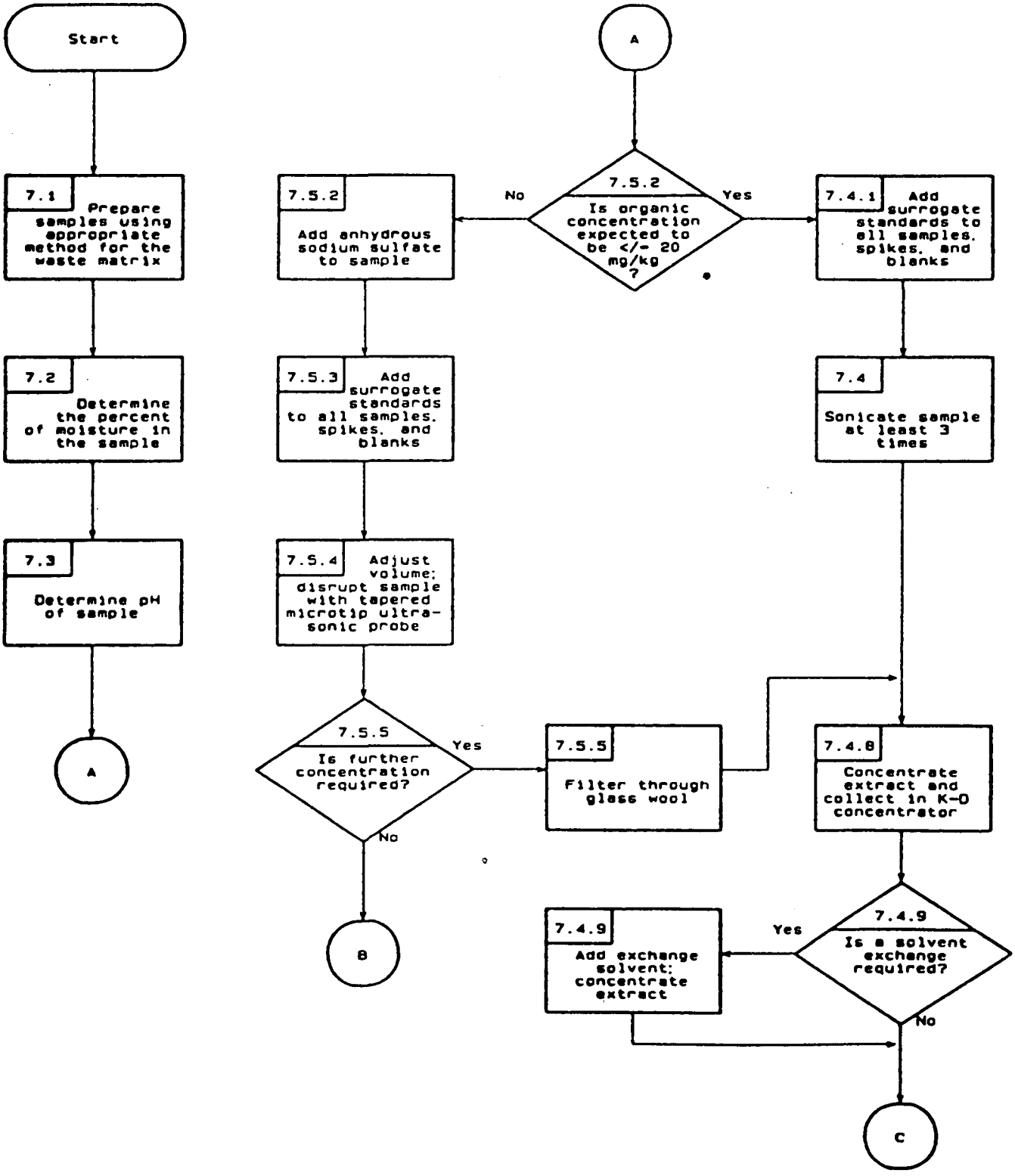
9.0 METHOD PERFORMANCE

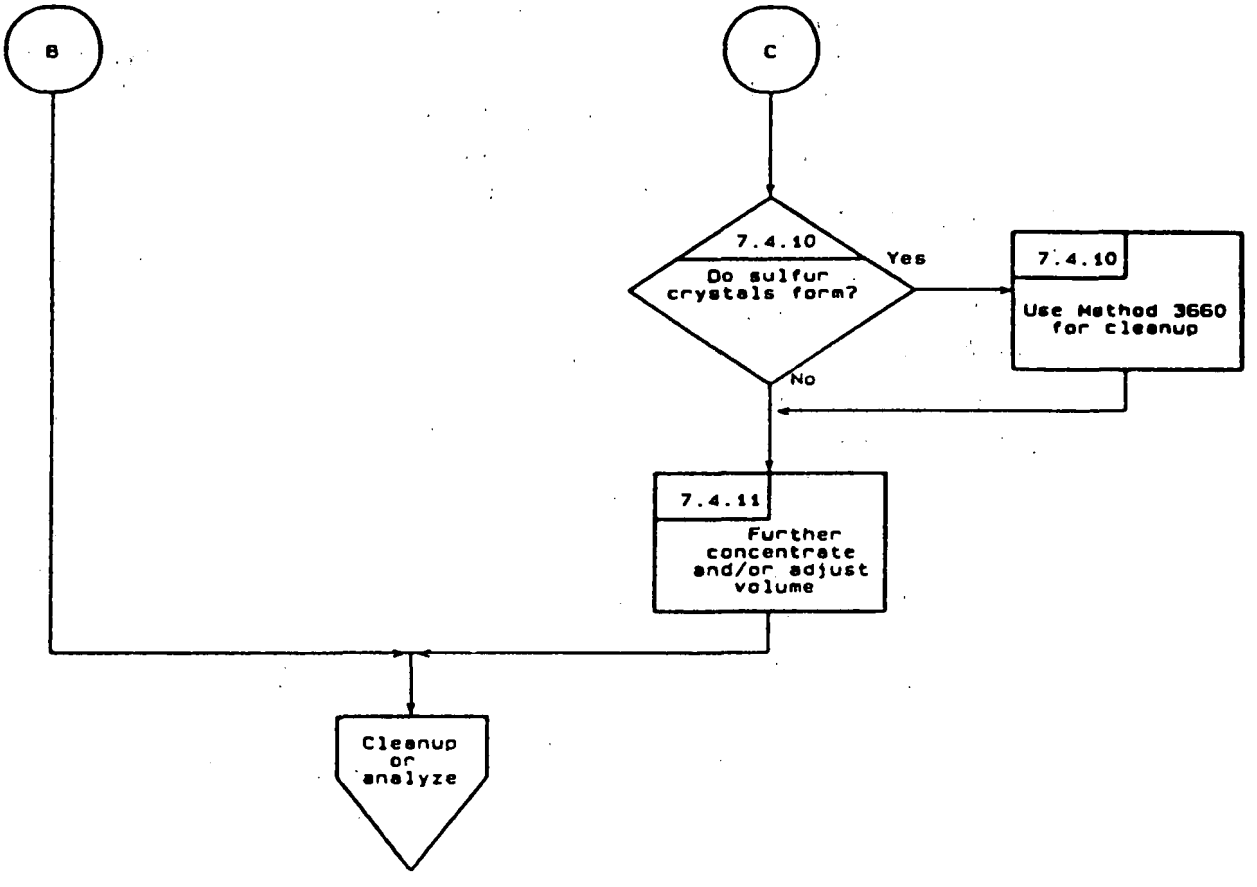
9.1 Refer to the determinative methods for performance data.

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. 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.


Start
7.1 Prepare samples using appropriate method for the waste matrix
7.2 Determine the percent of moisture in the sample
7.3 Determine pH of sample
A
A
7.5.2 Is organic concentration expected to be </- 20 mg/kg ?
No
Yes
7.5.2 Add anhydrous sodium sulfate to sample
7.5.3 Add surrogate standards to all samples, spikes, and blanks
7.5.4 Adjust volume; disrupt sample with tapered microtip ultra-sonic probe
7.5.5 Is further concentration required?
Yes
No
B
7.5.5 Filter through glass wool
7.4.1 Add surrogate standards to all samples, spikes, and blanks
7.4 Sonicate sample at least 3 times
7.4.8 Concentrate extract and collect in K-D concentrator
7.4.9 Is a solvent exchange required?
Yes
No
7.4.9 Add exchange solvent; concentrate extract
C


B
C
7.4.10
Do sulfur crystals form?
Yes
No
7.4.10
Use Method 3660 for cleanup
7.4.11
Further concentrate and/or adjust volume
Cleanup or analyze

METHOD 3580

WASTE DILUTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a solvent dilution of a non-aqueous waste sample prior to cleanup and/or analysis. It is designed for wastes that may contain organic chemicals at a level greater than 20,000 mg/kg and that are soluble in the dilution solvent.

1.2 It is recommended that an aliquot of the diluted sample be cleaned up. See the Cleanup section of this chapter for methods (Section 4.2.2).

2.0 SUMMARY OF METHOD

2.1 One gram of sample is weighed into a capped tube, and the sample is diluted to 10.0 mL with an appropriate solvent.

3.0 INTERFERENCES

3.1 Refer to Method 3500.

4.0 APPARATUS AND MATERIALS

4.1 Glass scintillation vials: At least 20-mL, with Teflon or aluminum-foil-lined screw-cap.

4.2 Spatula: Stainless steel or Teflon.

4.3 Balance: Capable of weighing 100 g to the nearest 0.01 g.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Disposable pipets: Pasteur.

4.6 Test tube rack.

4.7 Pyrex glass wool.

4.8 Volumetric flasks: 10-mL (optional).

5.0 REAGENTS

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

5.2 Solvents: Methylene chloride and hexane (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 Samples consisting of multiphases must be prepared by the phase separation method (Chapter Two) before extraction.

7.2 The sample dilution may be performed in a 10-mL volumetric flask. If disposable glassware is preferred, the 20-mL scintillation vial may be calibrated for use. Simply pipet 10.0 mL of extraction solvent into the scintillation vial and mark the bottom of the meniscus. Discard this solvent.

7.3 Transfer approximately 1 g of each phase (record weight to the nearest 0.1 g) of the sample to separate 20-mL vials or 10-mL volumetric flasks. Wipe the mouth of the vial with a tissue to remove any sample material. Cap the vial before proceeding with the next sample to avoid any cross-contamination.

7.4 Add 2.0 mL surrogate spiking solution to all samples and blanks. 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/uL of each base/neutral analyte and 400 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. See Method 3500 for details on the surrogate standard and matrix spiking solutions.

7.5 Immediately dilute to 10 mL with the appropriate solvent. For compounds to be analyzed by GC/ECD, e.g., organochlorine pesticides and PCBs, the dilution solvent should be hexane. For base/neutral and acid semivolatile priority pollutants, use methylene chloride. If dilution is to be cleaned up by gel permeation chromatography (Method 3640), use methylene chloride as the dilution solvent for all compounds.

7.6 Add 2.0 g of anhydrous sodium sulfate to the sample.

7.7 Cap and shake the sample for 2 min.

7.8 Loosely pack disposable Pasteur pipets with 2-3 cm glass wool plugs. Filter the extract through the glass wool and collect 5 mL of the extract in a tube or vial.

7.9 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 and matrix spike samples should be subjected to exactly the same analytical procedures as those used on actual samples.

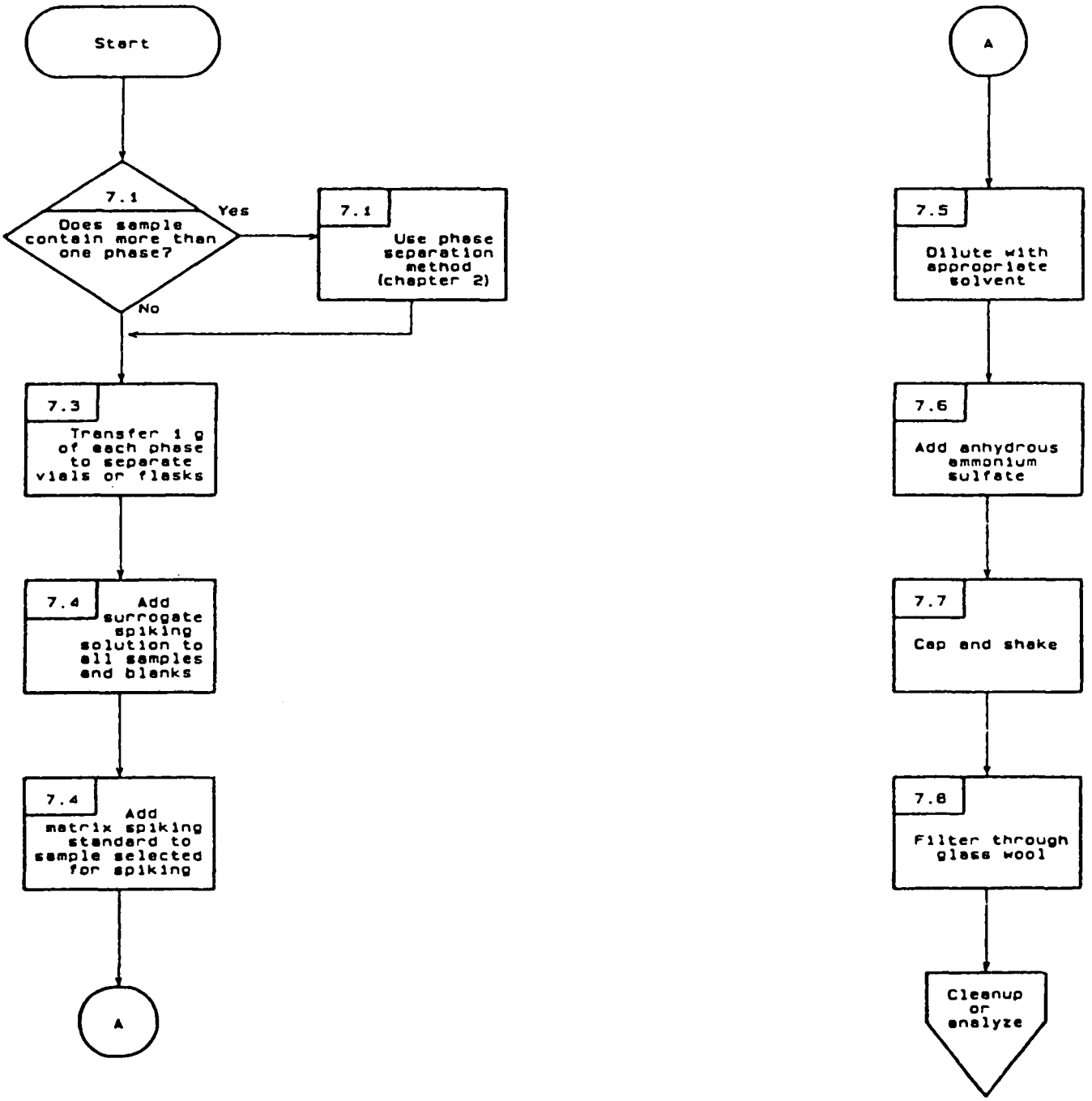
8.2 Refer to Chapter One for specific quality control procedures and Method 3500 for extraction and sample preparation procedures.

9.0 METHOD PERFORMANCE

9.1 Refer to the determinative methods for performance data.

10.0 REFERENCES

10.1 None applicable.


Start
7.1
Does sample contain more than one phase?
Yes
No
7.1
Use phase separation method (chapter 2)
7.3
Transfer 1 g of each phase to separate vials or flasks
7.4
Add surrogate spiking solution to all samples and blanks
7.4
Add matrix spiking standard to sample selected for spiking
A
A
7.5
Dilute with appropriate solvent
7.6
Add anhydrous ammonium sulfate
7.7
Cap and shake
7.8
Filter through glass wool
Cleanup or analyze

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, 8020, 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 (vapor pressure is approximately equal to mm Hg @ 25°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 screw-caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner.

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 min 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.

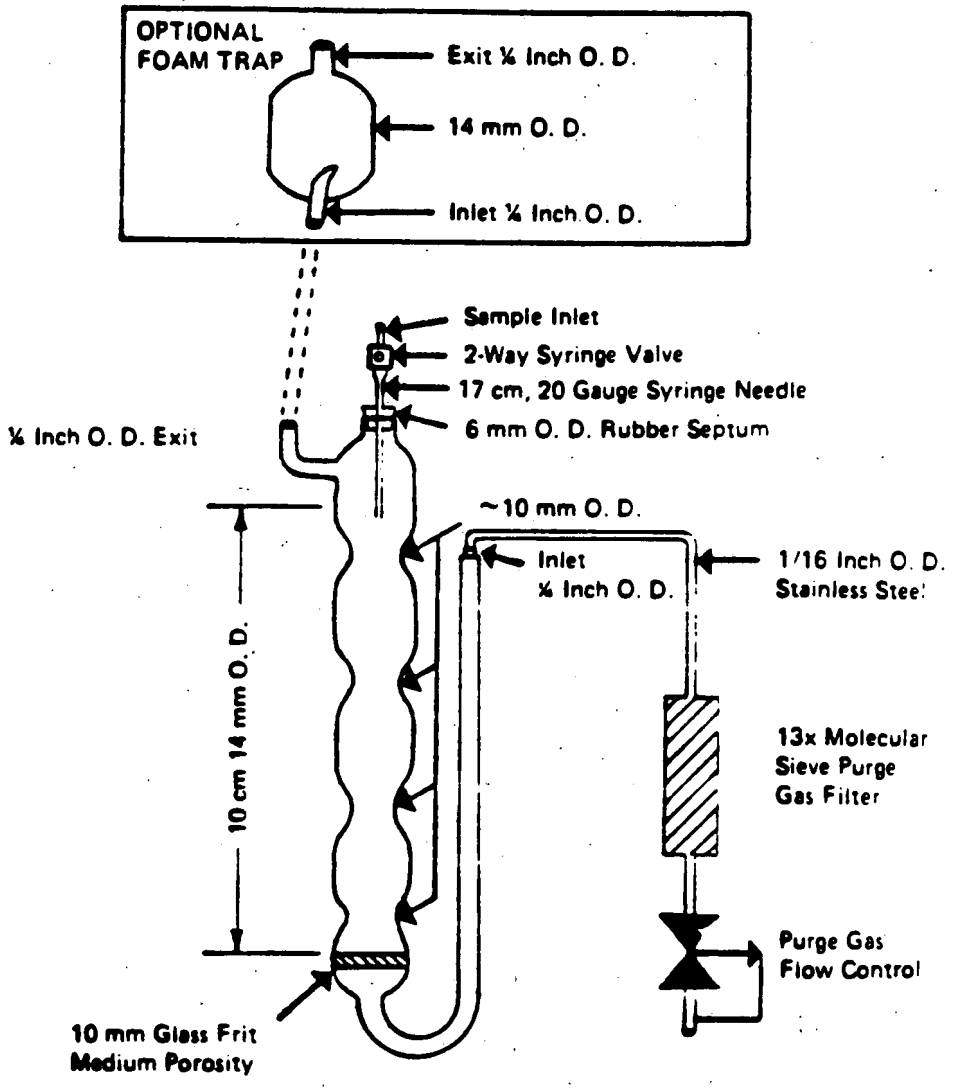


Figure 1. Purging chamber.

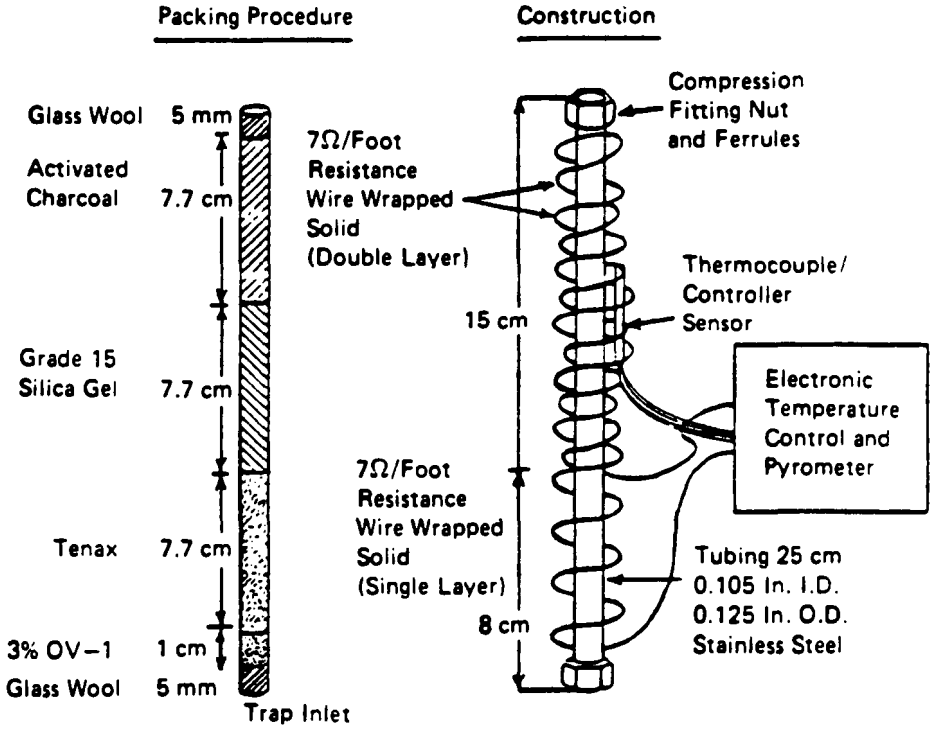


Figure 2. Trap packings and construction for Method 8010.

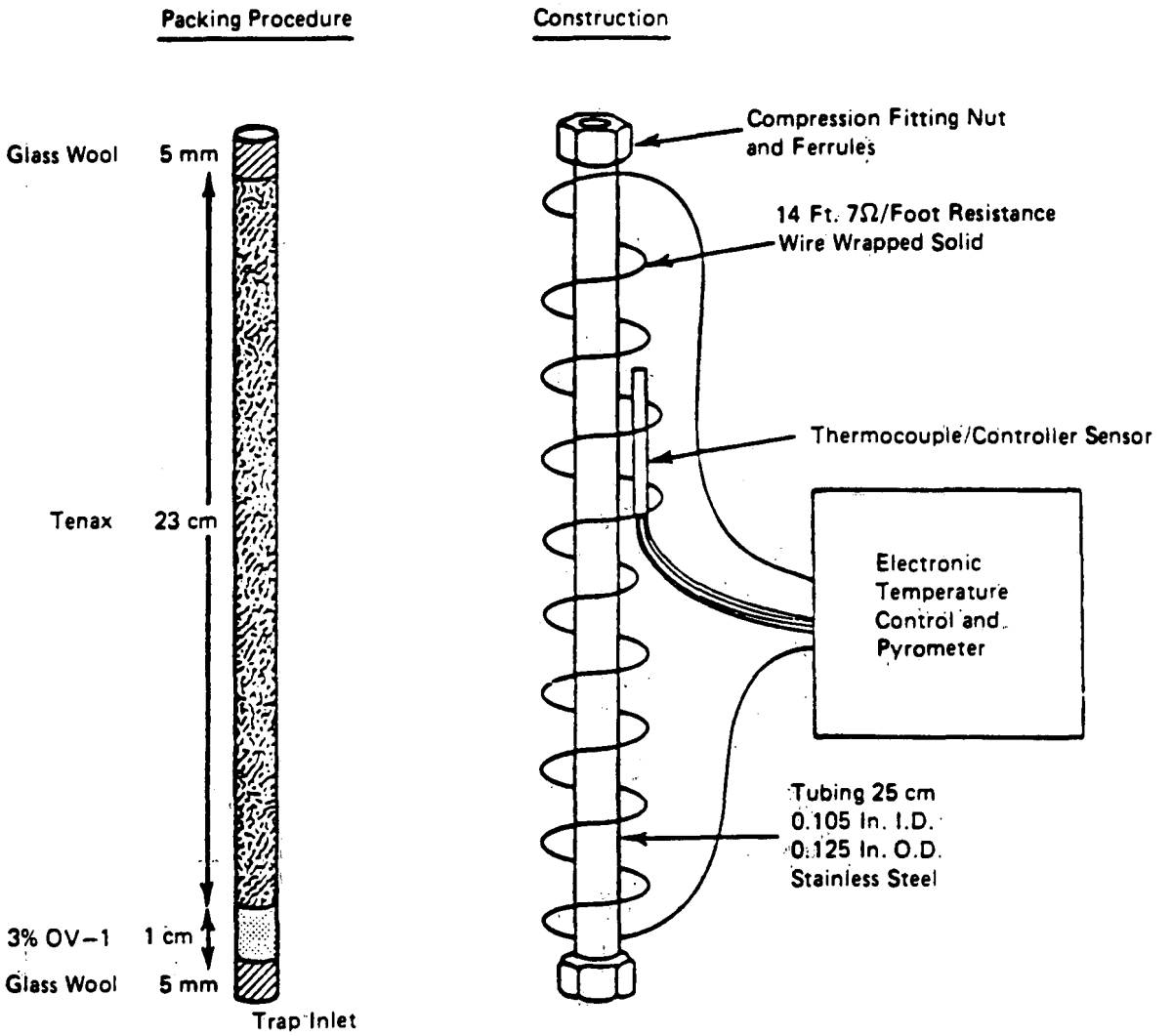


Figure 3. Trap packing and construction for Methods 8020 and 8030.

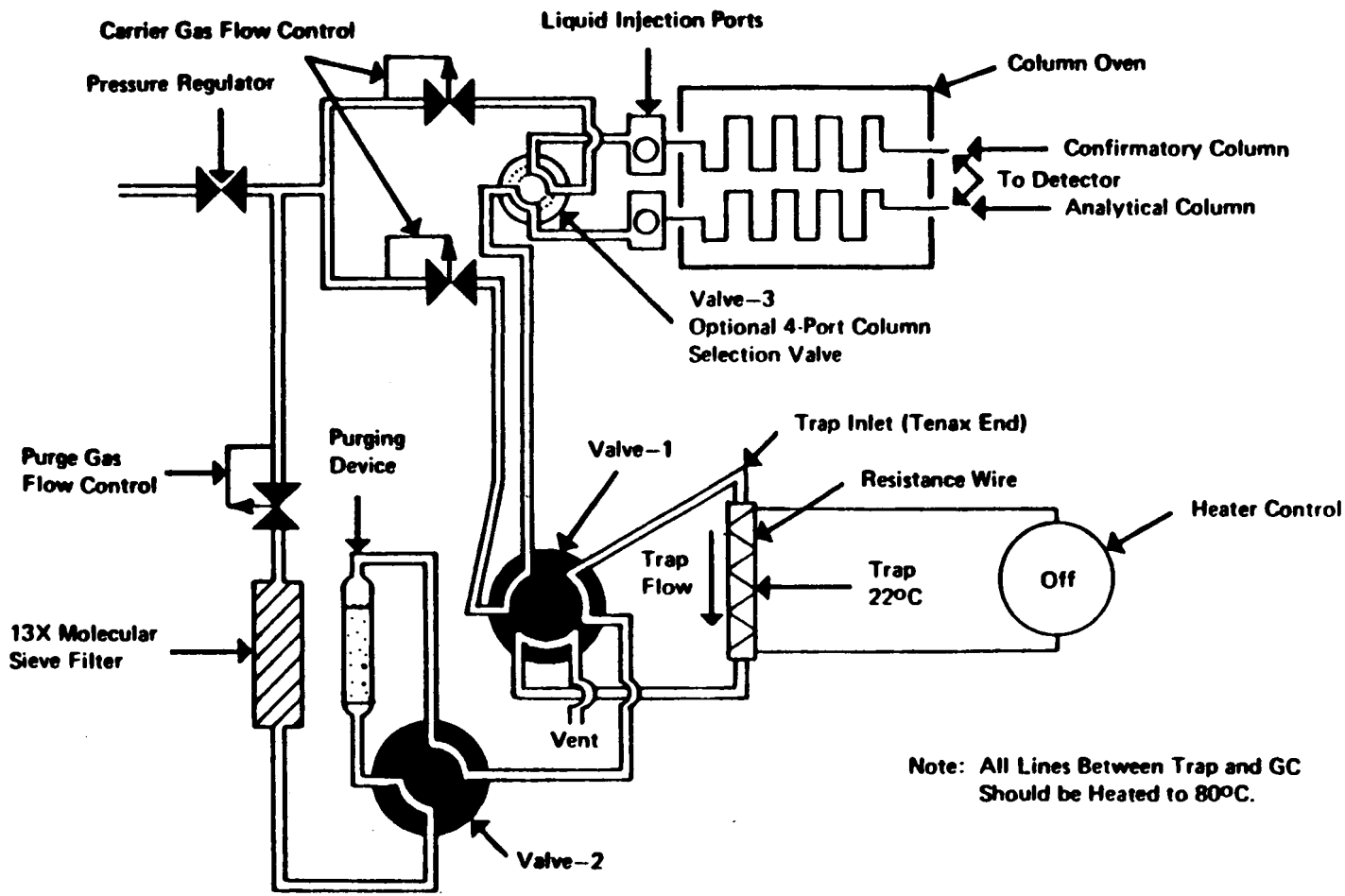


Figure 4. Purge-and-trap system, purge-sorb mode, for Methods 8010, 8020, and 8030.

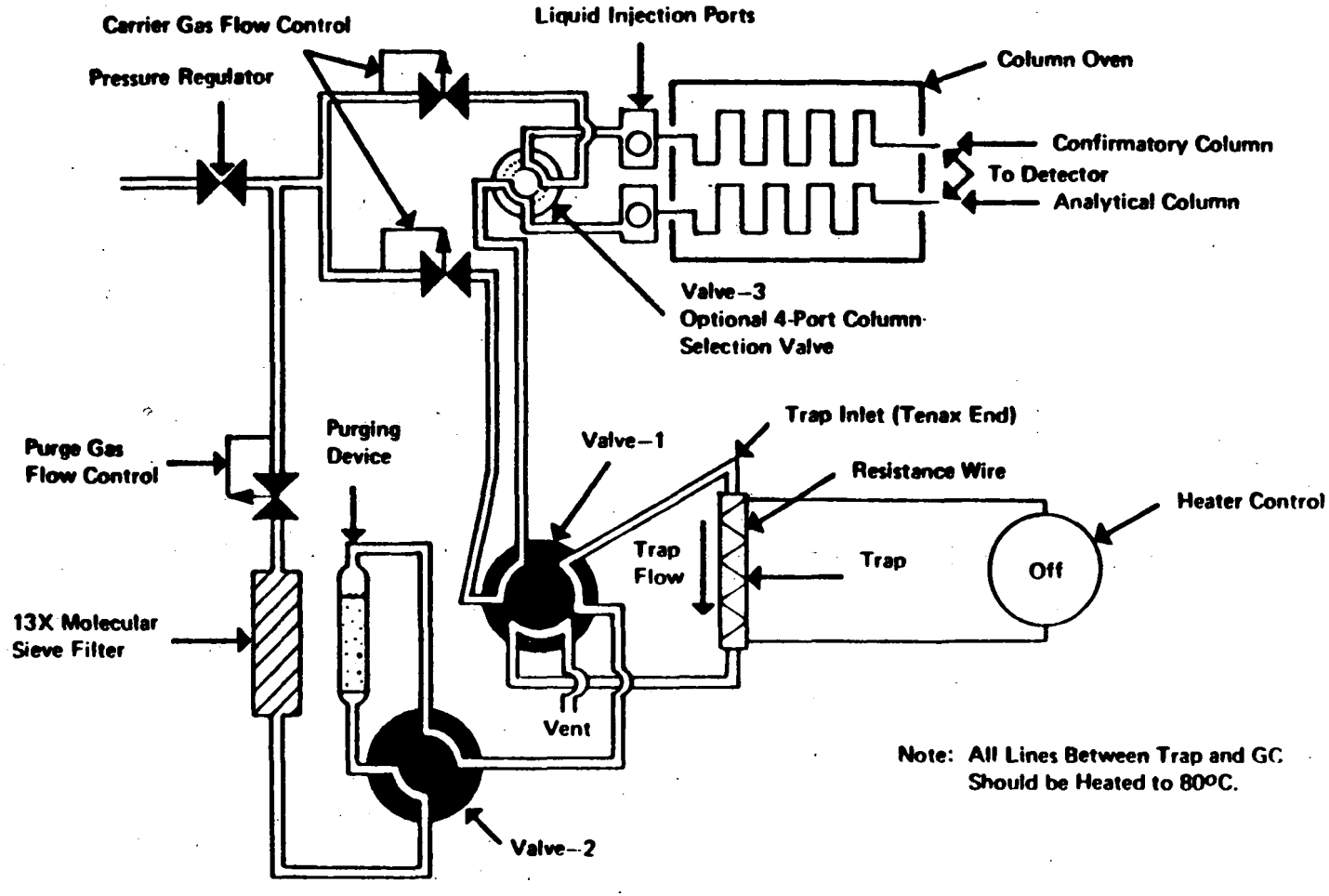


Figure 5. Purge-and-trap system, desorb mode, for Methods 8010, 8020, and 8030.

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: Should be 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 water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.1.1 Reagent water may be generated by passing trap water through a carbon filter bed containing about 500 g of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

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

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

5.2 Methanol: Pesticide quality or equivalent. Store away from other solvents.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 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, Section 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 Section 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 min 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. Add 5.0 mL of reagent water to the purging device. The reagent 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-uL or 25-uL microsyringe equipped with a long needle (Paragraph 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 microsyringe, be sure that the end of the syringe needle is well beneath the surface of the reagent water. Similarly, add 10 uL 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, Section 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:

7.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.1.6.2 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.

7.1.6.3 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, Sections 7.4.2.3 and 7.4.3.4 for details on continuing calibration.

TABLE 1. PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method			
	8010	8015	8020	8030
Purge gas	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium	Nitrogen or Helium
Purge gas flow rate (mL/min)	40	20	40	20
Purge time (min)	11.0 ± 0.1	15.0 ± 0.1	12.0 ± 0.1	15.0 ± 0.1
Purge temperature (°C)	Ambient	85 ± 2	Ambient	85 ± 2
Desorb temperature (°C)	180	180	180	180
Backflush inert gas flow (mL/min)	20-60	20-60	20-60	20-60
Desorb time (min)	4	1.5	4	1.5

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, Section 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 hr. 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 reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.3.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 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 Paragraph 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 reagent water (or methanol followed by reagent 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 sec; 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 min, 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 reagent 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 reagent 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 reagent 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 reagent water by adding at least 20 uL, but not more than 100-uL 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 Paragraph 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 reagent 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 Paragraph 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:

$$\frac{\text{g of sample - g of dry sample}}{\text{g of sample}} \times 100 = \% \text{ moisture}$$

7.3.3.1.6 Add the spiked reagent 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 Paragraphs 7.3.1.11-7.3.1.15. Use 5 mL of the same reagent 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. An aliquot of the extract is added to reagent 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 waste 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 Paragraph 7.3.3.1.5. For waste that is soluble in methanol, 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 methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.3.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

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 reagent methanol 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 methanol extract to reagent water.

7.3.3.2.5 Table 2 can be used to determine the volume of methanol extract to add to the 5 mL of reagent 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 uL. 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 reagent 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 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.3.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol 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/methanol 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 uL of methanol 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 Paragraph 7.3.3.2.6).

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.

[a]The 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.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.4 Sample analysis:

7.4.1 The samples prepared by this method may be analyzed by Methods 8010, 8015, 8020, 8030, and 8240. 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 reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

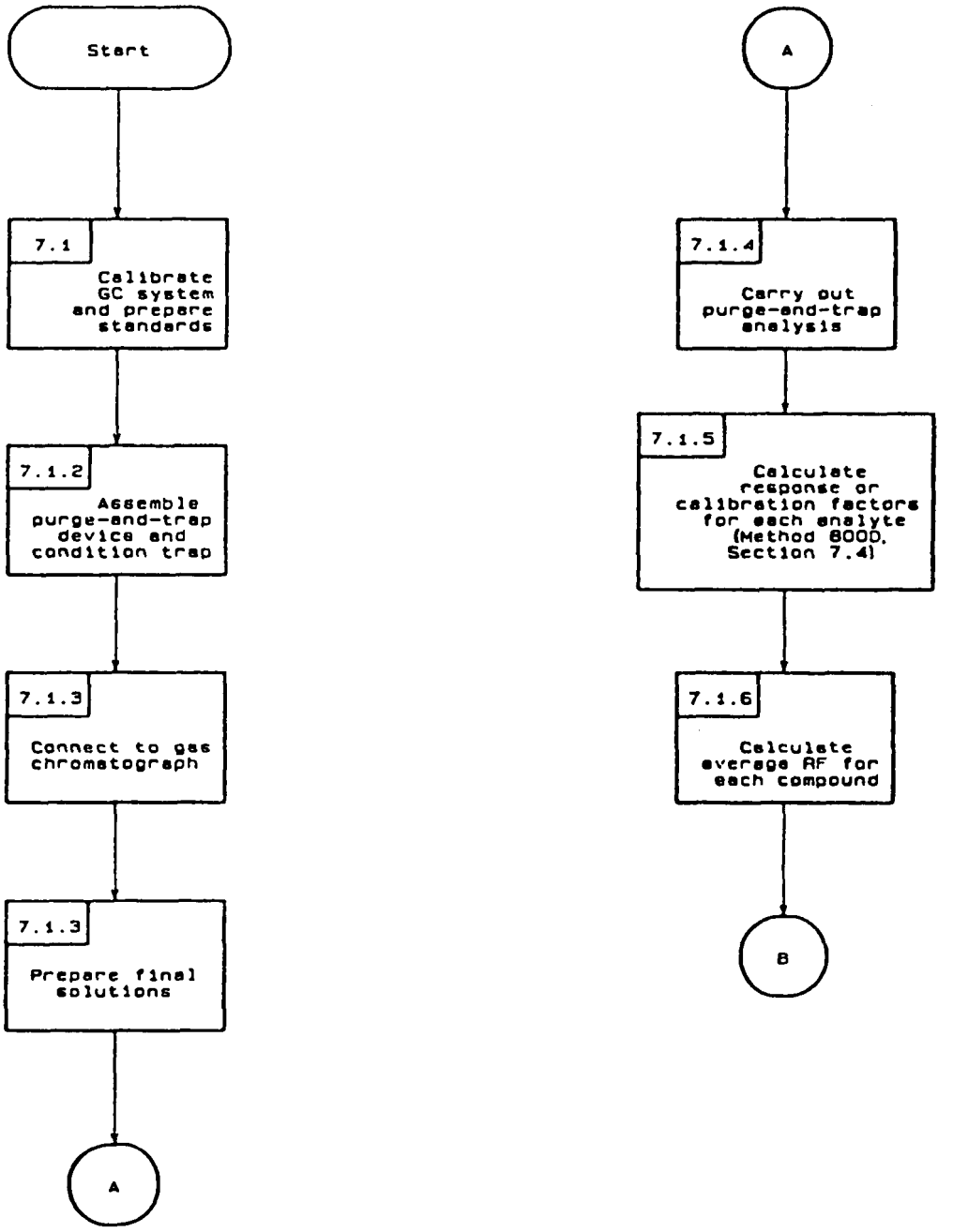
8.3 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified samples do not indicate sufficient sensitivity to detect <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.

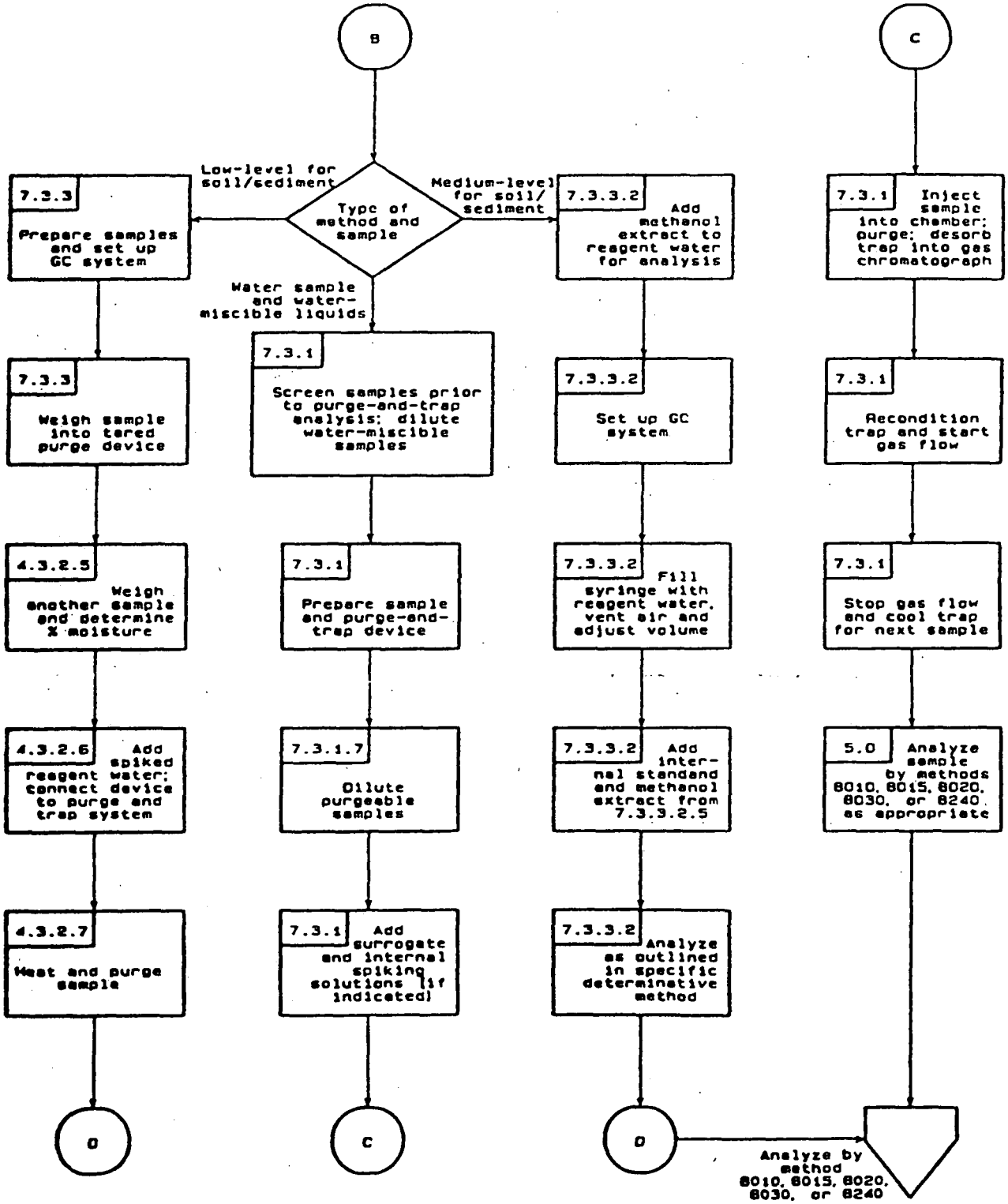
9.0 METHOD PERFORMANCE

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.


Start
7.1
Calibrate GC system and prepare standards
7.1.2
Assemble purge-and-trap device and condition trap
7.1.3
Connect to gas chromatograph
7.1.3
Prepare final solutions
A
A
7.1.4
Carry out purge-and-trap analysis
7.1.5
Calculate response or calibration factors for each analyte (Method 8000, Section 7.4)
7.1.6
Calculate average RF for each compound
B


B
C
Type of method and sample
Low-level for soil/sediment
Medium-level for soil/ sediment
Water sample and water-miscible liquids
7.3.3 Prepare samples and set up GC system
7.3.3.2 Add methanol extract to reagent water for analysis
7.3.1 Inject sample into chamber; purge; desorb trap into gas chromatograph
7.3.3 Weigh sample into tared purge device
7.3.1 Screen samples prior to purge-and-trap analysis; dilute water-miscible samples
7.3.3.2 Set up GC system
7.3.1 Recondition trap and start gas flow
4.3.2.5 Weigh another sample and determine % moisture
7.3.1 Prepare sample and purge-and-trap device
7.3.3.2 Fill syringe with reagent water, vent air and adjust volume
7.3.1 Stop gas flow and cool trap for next sample
4.3.2.6 Add spiked reagent water; connect device to purge and trap system
7.3.1.7 Dilute purgeable samples
7.3.3.2 Add internal standard and methanol extract from 7.3.3.2.5
5.0 Analyze sample by methods 8010, 8015, 8020, 8030, or 8240, as appropriate
4.3.2.7 Heat and purge sample
7.3.1 Add surrogate and internal spiking solutions (if indicated)
7.3.3.2 Analyze as outlined in specific determinative method
D
C
D
Analyze by method 8010, 8015, 8020, 8030, or 8240

METHOD 5040

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES FROM VOLATILE ORGANIC SAMPLING TRAIN

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 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.

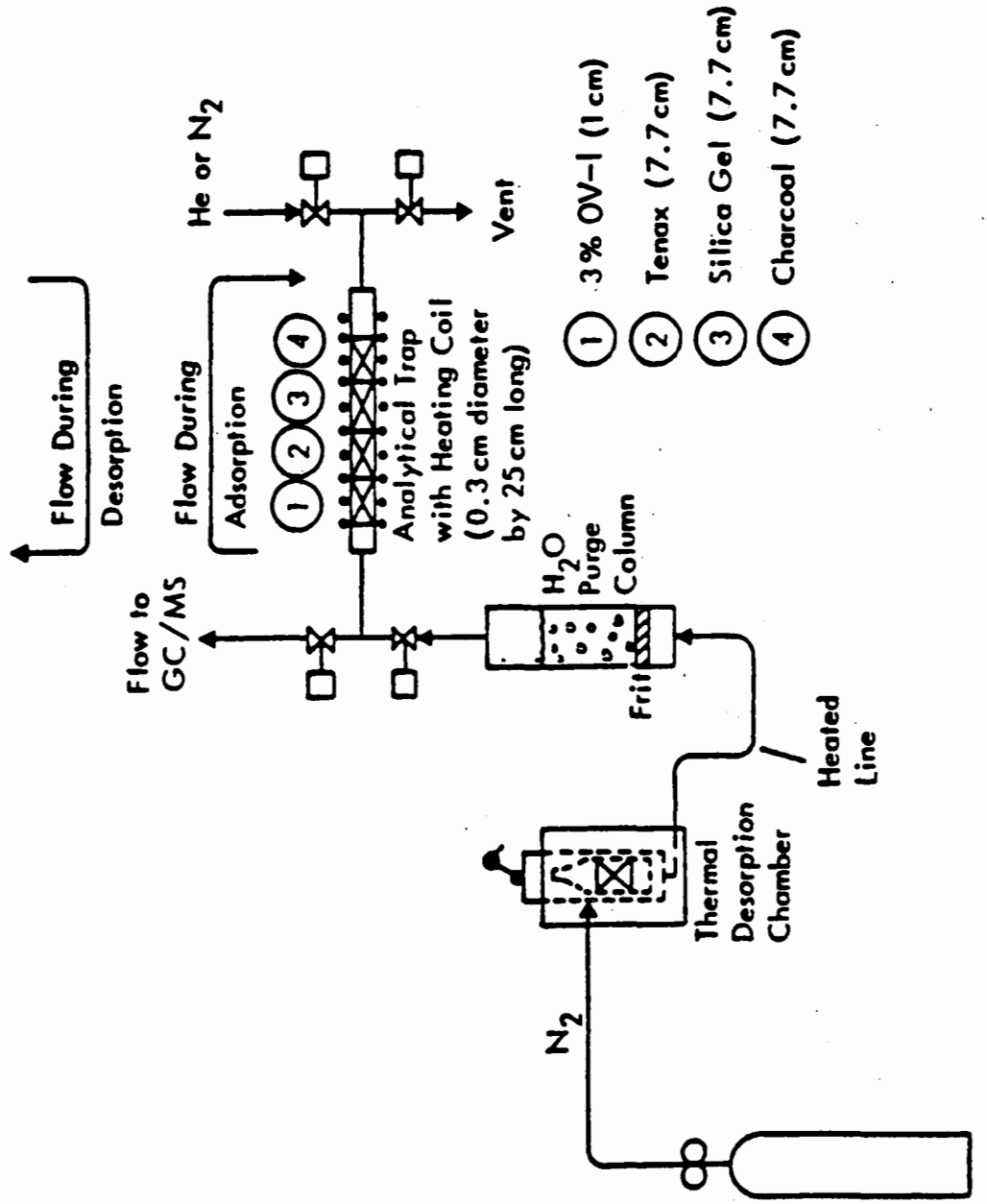


Figure 1. Schematic diagram of trap desorption/analysis system.

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 ± 10°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 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the parameters of interest.

5.1.1 Reagent water may be generated by passing tap water through a carbon filter bed containing about 450 g of activated carbon (Calgon Corporation, Filtrasorb-300, or equivalent).

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

5.1.3 Reagent water may also be prepared by boiling distilled water for 15 min. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hr. Allow the water to cool to room temperature while continuing to bubble the inert gas through the water. This water should be transferred directly to the purge-and-trap apparatus for use.

5.1.4 Other methods that can be shown to produce organic-free water can be used.

5.2 Analytical trap reagents:

5.2.1 **2,6-Diphenylene oxide polymer:** Tenax (60/80 mesh), chromatographic grade or equivalent.

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

5.2.3 **Silica gel:** Davison Chemical (35/00 mesh), Grade 15, or equivalent.

5.2.4 **Charcoal:** Petroleum-based (SKC Lot 104 or equivalent).

5.3 Stock standard solution:

5.3.1 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.

5.3.2 Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of <35°C. All other standards must be replaced monthly, or sooner if comparison with check standards indicates a problem.

5.4 Secondary dilution standards:

5.4.1 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.

5.5 4-Bromofluorobenzene (BFB) standard:

5.5.1 Prepare a 25 ng/uL solution of BFB in methanol.

5.6 Deuterated benzene:

5.6.1 Prepare a 25 ng/uL 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-uL syringe with clean methanol and drawing air into the syringe to the 1.0-uL mark. This is followed by drawing a methanolic solution of the calibration standards (containing 25 ug/uL of the internal standard) to the 2.0-uL 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 response factor (RF) for each compound, using Equation 1.

$$RF = A_S C_{is} / A_{is} C_S \quad (1)$$

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 ±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 identification:

7.4.1 The procedure for qualitative identification of volatile POHCs using this protocol is described in Method 8240.

7.5 Calculations:

7.5.1 When an analyte has been qualitatively identified, quantification 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 Paragraph 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. These values should then be blank corrected. Guidelines for blank correction of sample cartridges are outlined below.

7.5.1.3.1 After all blanks (field and trip) are analyzed, a paired t-test should be used to determine whether trip blanks are significantly different from field blanks. If no difference is found, then the mean and standard deviation of the combined field and trip blanks for each POHC of interest is calculated.

7.5.1.3.2 If, when using the paired t-test, the field and trip blanks are determined to be different, then the field blank (or the mean of multiple field blanks) associated with a particular run should be used as the blank value for that particular run.

7.5.1.4 Next, for each sample/POHC combination, a determination must be made as to whether a particular sample is significantly different from the associated blank. If the mean of the trip and field blanks is used, then a sample is different from the blank if:

$$(\text{measured sample value}) - (\text{mean blank value}) > (3 \times \text{blank standard deviation})$$

(If an individual field blank is used as the blank value, the above criteria do not apply.) If the sample is determined to be different from the blank according to the above criteria, then the emission value of a particular POHC is blank-corrected by subtracting the mean blank value from the measured sample value.

7.5.1.5 If, according to the above procedures, the sample cannot be distinguished from the blank (i.e., for a given POHC there is a high sample value and high blank value or there is a low sample value and low blank value), the measured sample value is not blank-corrected. In this case, the measured sample value is used to calculate a maximum emission value (and therefore a minimum DRE value) for that particular run.

7.5.1.6 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.

7.5.1.7 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.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3500 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 Paragraph 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 Paragraph 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:

Upper Control Limit (UCL) = A + 3S.
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 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

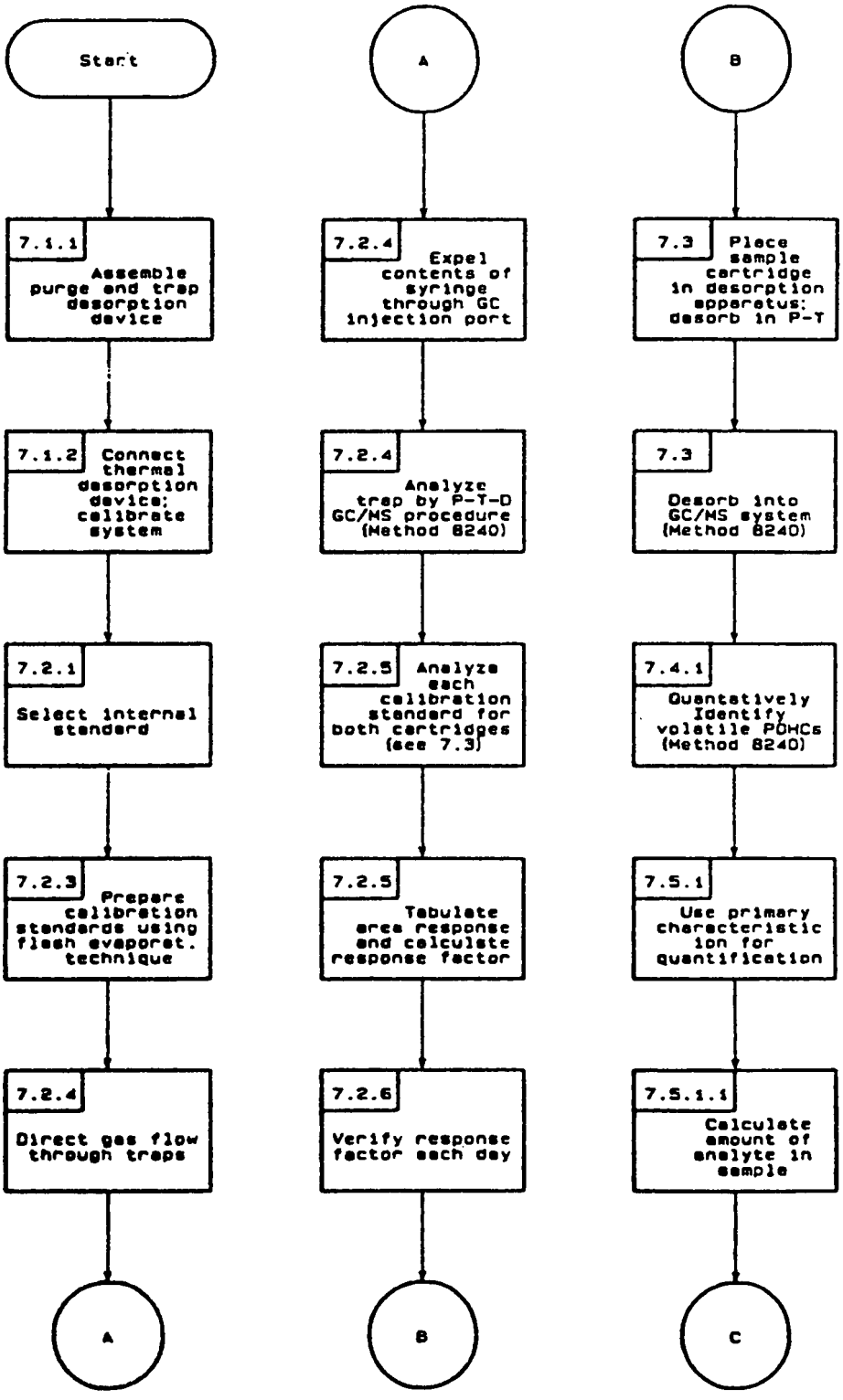
1. Protocol for Collection and Analysis of Volatile POHC's Using VOST. EPA/600/8-84-007, March 1984.

2. Validation of the Volatile Organic Sampling Train (VOST) Protocol. Volumes I and II. EPA/600/4-86-014a, January 1986.

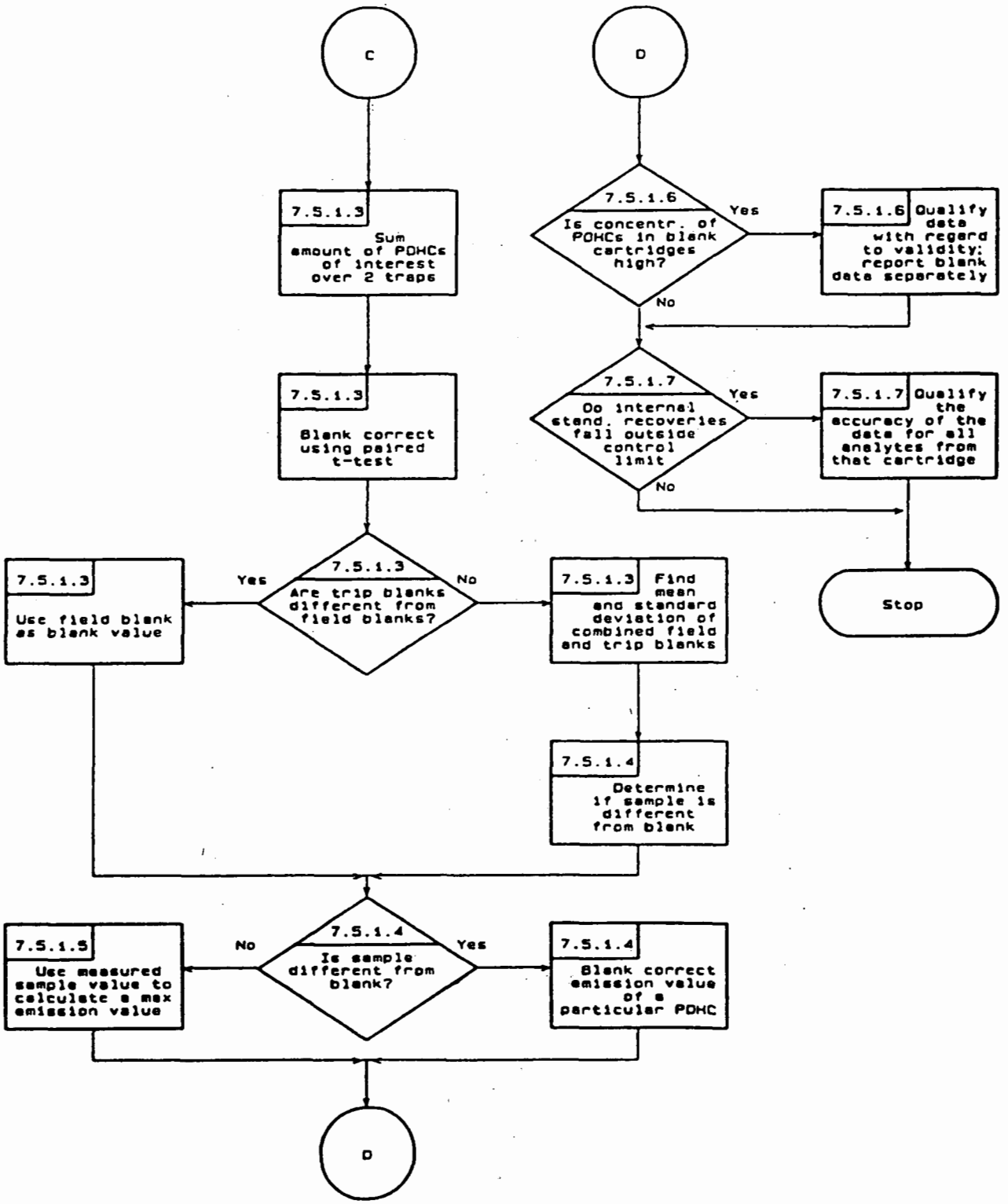
METHOD 5040

PROTOCOL FOR ANALYSIS OF SORBENT CARTRIDGES

FROM VOLATILE ORGANIC SAMPLING TRAIN



Revision 0
Date September 1986


C
D
7.5.1.3
Sum amount of PDHCs of interest over 2 traps
7.5.1.6
Is concentr. of PDHCs in blank cartridges high?
Yes
No
7.5.1.6 Qualify data with regard to validity; report blank data separately
7.5.1.3
Blank correct using paired t-test
7.5.1.7
Do internal stand. recoveries fall outside control limit
Yes
No
7.5.1.7 Qualify the accuracy of the data for all analytes from that cartridge
Stop
7.5.1.3
Are trip blanks different from field blanks?
Yes
No
7.5.1.3
Use field blank as blank value
7.5.1.3 Find mean and standard deviation of combined field and trip blanks
7.5.1.4
Determine if sample is different from blank
7.5.1.4
Is sample different from blank?
No
Yes
7.5.1.5
Use measured sample value to calculate a max emission value
7.5.1.4
Blank correct emission value of a particular PDHC
D

4.2 SAMPLE PREPARATION METHODS

4.2.2 CLEANUP

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, Section 4.1.

7.0 PROCEDURE

7.1 Prior to using the cleanup procedures, samples should undergo solvent extraction. Chapter Two, Section 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 Section 4.3 of this chapter. If the analytes of interest are not able to be determined due to interferences, cleanup is performed.

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, 3640
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.

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 (Section 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, and duplicates) must also be processed through the same cleanup procedure.

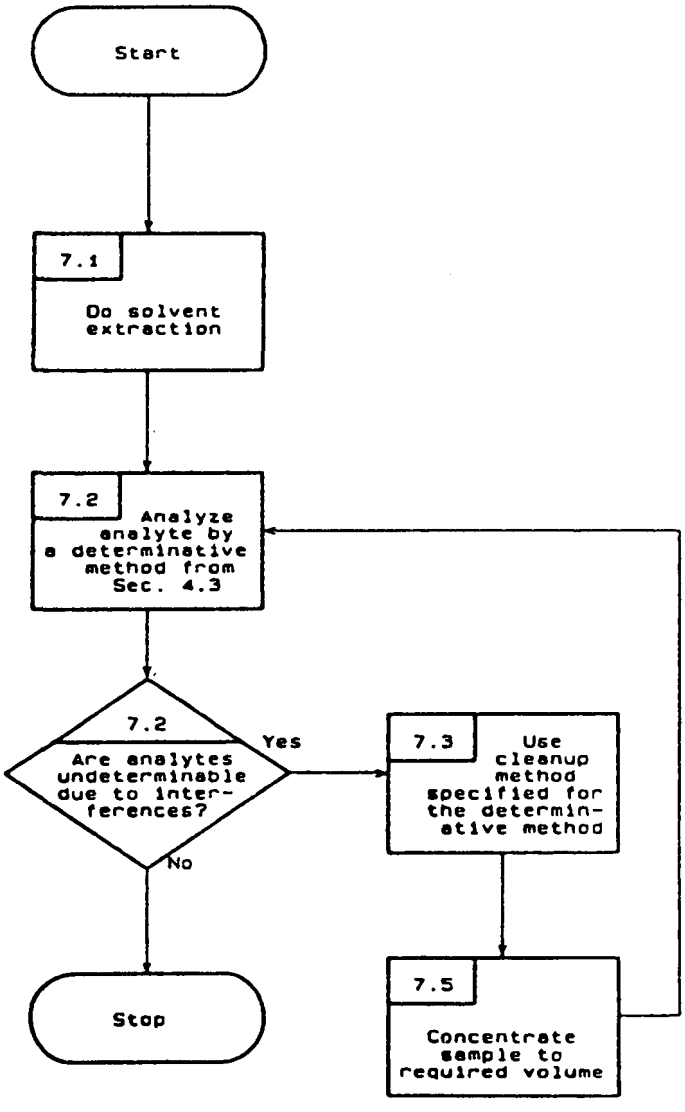
8.3 The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and 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.


Start
7.1
Do solvent extraction
7.2
Analyze analyte by a determinative method from Sec. 4.3
7.2
Are analytes undeterminable due to interferences?
Yes
No
7.3
Use cleanup method specified for the determinative method
7.5
Concentrate sample to required volume
Stop

METHOD 3610

ALUMINA COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 **Basic** (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 **Neutral** (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 **Acidic** (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 **Activity grades**: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of H_2O to Grade 1 (prepared by heating at 400-450°C until no more H_2O is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing phthalate esters and nitrosamines. For alumina column cleanup of petroleum wastes, see Method 3611.

2.0 SUMMARY OF METHOD

2.1 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.

3.0 INTERFERENCES

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

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

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300-mm x 10-mm I.D., 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 Reagent bottle: 500-mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.5.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Vials: Glass, 2-mL capacity, with Teflon-lined screw cap.

4.9 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

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

5.2 Eluting solvents:

5.2.1 **Diethyl ether:** Pesticide quality or equivalent.

5.2.1.1 Must be free of peroxides, as indicated by EM Quant test strips (test strips are available from EM Laboratories Inc., 500 Executive Blvd., Elmsford, New York 10523).

5.2.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.2.2 **Methanol, pentane, hexane, methylene chloride:** Pesticide quality or equivalent.

5.3 Alumina:

5.3.1 **For cleanup of phthalate extracts:** Alumina-Neutral, activity Super I, W200 series (ICN Life Sciences Group, No. 404583). To prepare for use, place 100 g of alumina into a 500-mL beaker and heat for approximately 16 hr at 400°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool, add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. Keep the bottle sealed tightly.

5.3.2 **For cleanup of nitrosamine extracts:** Alumina-Basic, activity Super I, W200 series (ICN Life Sciences Group, No. 404571, or equivalent). To prepare for use, place 100 g of alumina into a 500-mL reagent bottle and add 2 mL of reagent water. Mix the alumina preparation thoroughly by shaking or rolling for 10 min and let it stand for at least 2 hr. The preparation should be homogeneous before use. Keep the bottle sealed tightly to ensure proper activity.

5.4 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

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 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of alumina into a chromatographic column to settle alumina and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Pre-elute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 35 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 140 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned up extract to whatever volume is required (10.0 mL for Method 8060) and analyze. Compounds that elute in this fraction are as follows:

Bis(2-ethylhexyl) phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate.

7.2 Nitrosamines:

7.2.1 Reduce the sample extract to 2 mL prior to cleanup.

7.2.2 Diphenylamine, if present in the original sample extract, must be separated from the nitrosamines if N-nitrosodiphenylamine is to be determined by this method.

7.2.3 Place 12 g of the alumina preparation into a 10-mm I.D. chromatographic column. Tap the column to settle the alumina and add 1-2 cm of anhydrous sodium sulfate to the top.

7.2.4 Pre-elute the column with 10 mL of ethyl ether/pentane (3:7)(v/v). Discard the eluate (about 2 mL) and just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.5 Just prior to exposure of the sodium sulfate layer to the air, add 70 mL of ethyl ether/pentane (3:7)(v/v). Discard the first 10 mL of eluate. Collect the remainder of the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction contains N-nitroso-di-n-propylamine.

7.2.6 Next, elute the column with 60 mL of ethyl ether/pentane (1:1)(v/v), collecting the eluate in a second 500-mL K-D flask equipped with a 10-mL concentrator tube. Add 15 mL of methanol to the K-D flask. This fraction will contain N-nitrosodimethylamine, most of the N-nitroso-di-n-propylamine, and any diphenylamine that is present.

7.2.7 Concentrate both fractions, but use pentane to prewet the Snyder column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of pentane. Adjust the final volume to whatever is required in the appropriate determinative method (Section 4.3 of this chapter). Analyze the fractions.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

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

8.2 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 the determinative methods for performance data.

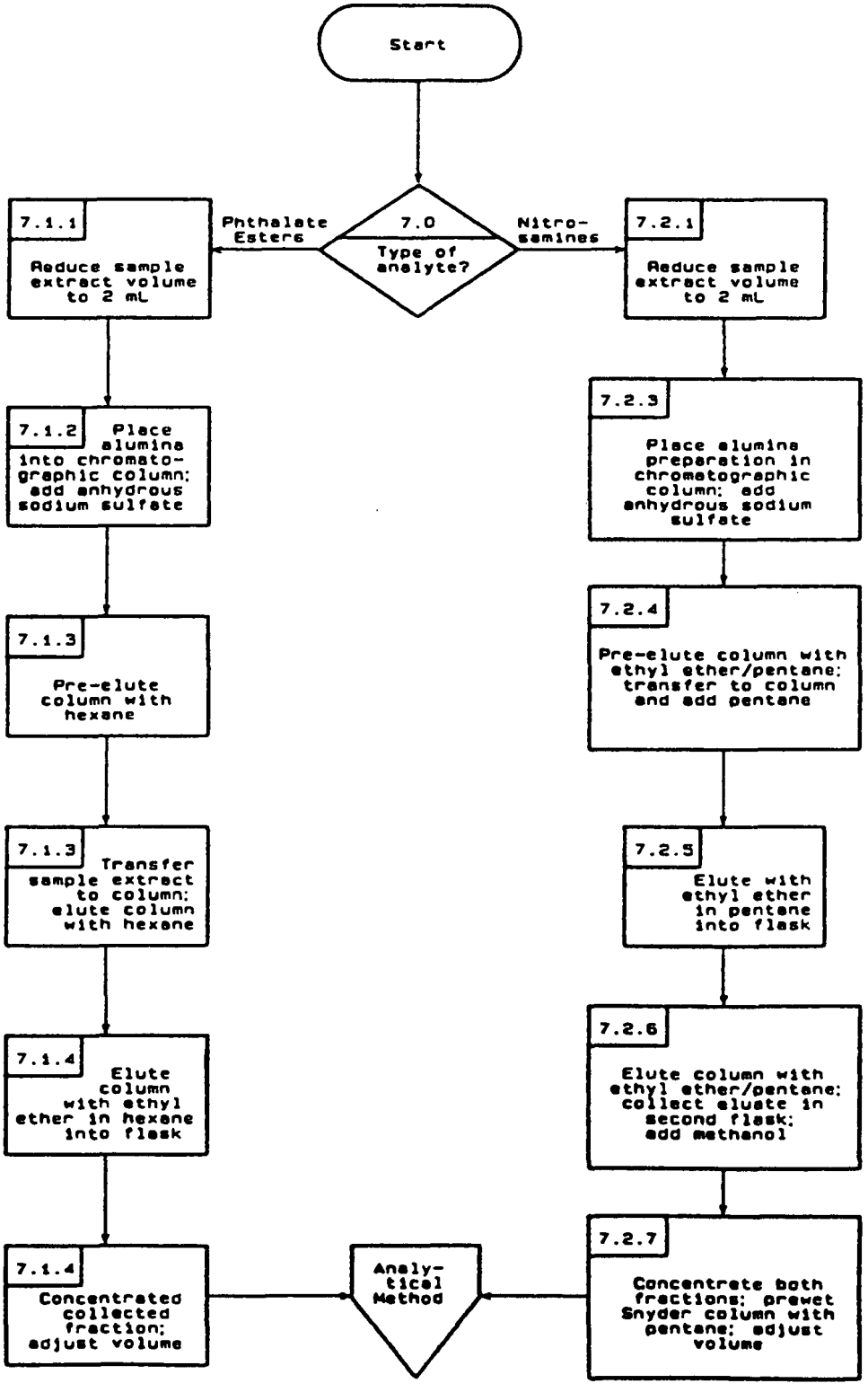
10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. 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.

METHOD 3610

ALUMINA COLUMN CLEANUP



Revision 0
Date September 1986

METHOD 3611

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES

1.0 SCOPE AND APPLICATION

1.1 Method 3611 was formerly Method 3570 in the Second Edition of this manual.

1.2 Scope: Alumina is a highly porous and granular form of aluminum oxide. It is available in three pH ranges (basic, neutral, and acidic) for use in column chromatography. It is used to separate analytes from interfering compounds of a different chemical polarity.

1.2 General Applications (Gordon and Ford):

1.2.1 **Basic** (B) pH (9-10): USES: Basic and neutral compounds stable to alkali, alcohols, hydrocarbons, steroids, alkaloids, natural pigments. DISADVANTAGES: Can cause polymerization, condensation, and dehydration reactions; cannot use acetone or ethyl acetate as eluants.

1.2.2 **Neutral** (N): USES: Aldehydes, ketones, quinones, esters, lactones, glycoside. DISADVANTAGES: Considerably less active than the basic form.

1.2.3 **Acidic** (A) pH (4-5): USES: Acidic pigments (natural and synthetic), strong acids (that otherwise chemisorb to neutral and basic alumina).

1.2.4 **Activity grades**: Acidic, basic, or neutral alumina can be prepared in various activity grades (I to V), according to the Brockmann scale, by addition of H_2O to Grade 1 (prepared by heating at 400-450°C until no more H_2O is lost). The Brockmann scale (Gordon and Ford, p. 374) is reproduced below:

Water added (wt. %):	0	3	6	10	15
Activity grade:	I	II	III	IV	V
RF (p-aminoazobenzene):	0.0	0.13	0.25	0.45	0.55

1.3 Specific applications: This method includes guidance for separation of petroleum wastes into aliphatic, aromatic, and polar fractions.

2.0 SUMMARY OF METHOD

2.1 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.

3.0 INTERFERENCES

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

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

3.3 Caution must be taken to prevent overloading of the chromatographic column. As the column loading for any of these types of wastes approaches 300 mg of extractable organics, separation recoveries will suffer. If overloading is suspected, an aliquot of the base-neutral extract prior to cleanup may be weighed and then evaporated to dryness. A gravimetric determination on the aliquot will indicate the weight of extractable organics in the sample.

4.0 APPARATUS AND MATERIALS

4.1 Chromatography column: 300-mm x 10-mm I.D., 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 Reagent bottle: 500-mL.

4.4 Muffle furnace.

4.5 Kuderna-Danish (K-D) apparatus:

4.5.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.5.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.5.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.5.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.6 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.7 Water bath: Heated with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

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

5.2 Eluting solvents: Methanol, hexane, methylene chloride (pesticide quality or equivalent).

5.3 Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 130°C prior to use.

5.4 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

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 suggested that Method 3650, Acid-Base Partition Cleanup, be performed on the sample extract prior to alumina cleanup.

7.2 Fill the glass chromatographic column to about 20 cm with hexane. Weigh out 10.0 g of alumina and add the alumina to the column. Gently tap the column to distribute the alumina evenly (minimize chromatographic voids). Alternatively, a slurry of alumina in hexane may be used to pack the column.

7.3 Allow the alumina to settle and then add 1.0 g of anhydrous sodium sulfate on top of the alumina.

7.4 Elute the column with 50 mL of hexane. Let the solvent flow through the column until the head of the liquid in the column is just above the sodium sulfate layer. Close the stopcock to stop solvent flow.

7.5 Transfer 1.0 mL of sample extract onto the column. Rinse out extract vial with 1 mL hexane and add it to the column immediately. To avoid overloading the column, it is suggested that no more than 300 mg of extractable organics be placed on the column (see Paragraph 3.3).

7.6 Just prior to exposure of the sodium sulfate to the air, elute the column with a total of 15 mL of hexane. If the extract is in 1 mL of hexane, and if 1 mL of hexane was used as a rinse, then 13 mL of additional hexane should be used. Collect the effluent in a 50-mL flask and label this fraction "base/neutral aliphatics." Adjust the flow rate to 2 mL/min.

7.7 Elute the column with 100 mL of methylene chloride and collect the effluent in a 250-mL flask. Label this fraction "base/neutral aromatics."

7.8 Elute the column with 100 mL of methanol and collect the effluent in a 250-mL flask. Label this fraction "base/neutral polars."

7.9 Concentrate the extracts by the standard K-D technique to whatever volume is required (1-10 mL) in the appropriate determinative method (Section 4.3 of this chapter). Analyze whichever fractions contain the analytes of interest.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds 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 The precision and accuracy of the method will depend upon the overall performance of the sample preparation and analysis.

9.2 A rag oil sample was analyzed by a number of laboratories according to the procedure outlined in this method. The results of these analyses for selected components in the rag oil are presented in Table 1. Reconstructed ion chromatograms from the GC/MS analyses are included as Figures 1 and 2.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. 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. RESULTS OF ANALYSIS FOR SELECTED COMPONENTS IN RAG OIL

Compound	Mean Conc. (ug/g)[a]	Standard Deviation	%RSD[b]
Naphthalene	216	42	19
Fluorene	140	66	47
Phenanthrene	614	296	18
2-Methylnaphthalene	673	120	18
Dibenzothiophene	1084	286	26
Methylphenanthrene	2908	2014	69
Methyldibenzothiophene	2200	1017	46
	Average Surrogate Recoveries		
Nitrobenzene-d_5	58.6	11	
Terphenyl-d_{14}	83.0	2.6	
Phenol-d_6	80.5	27.6	
Naphthalene-d_8	64.5	5.0	

[a] Based on five determinations from three laboratories.

[b] Percent Relative Standard Deviation.

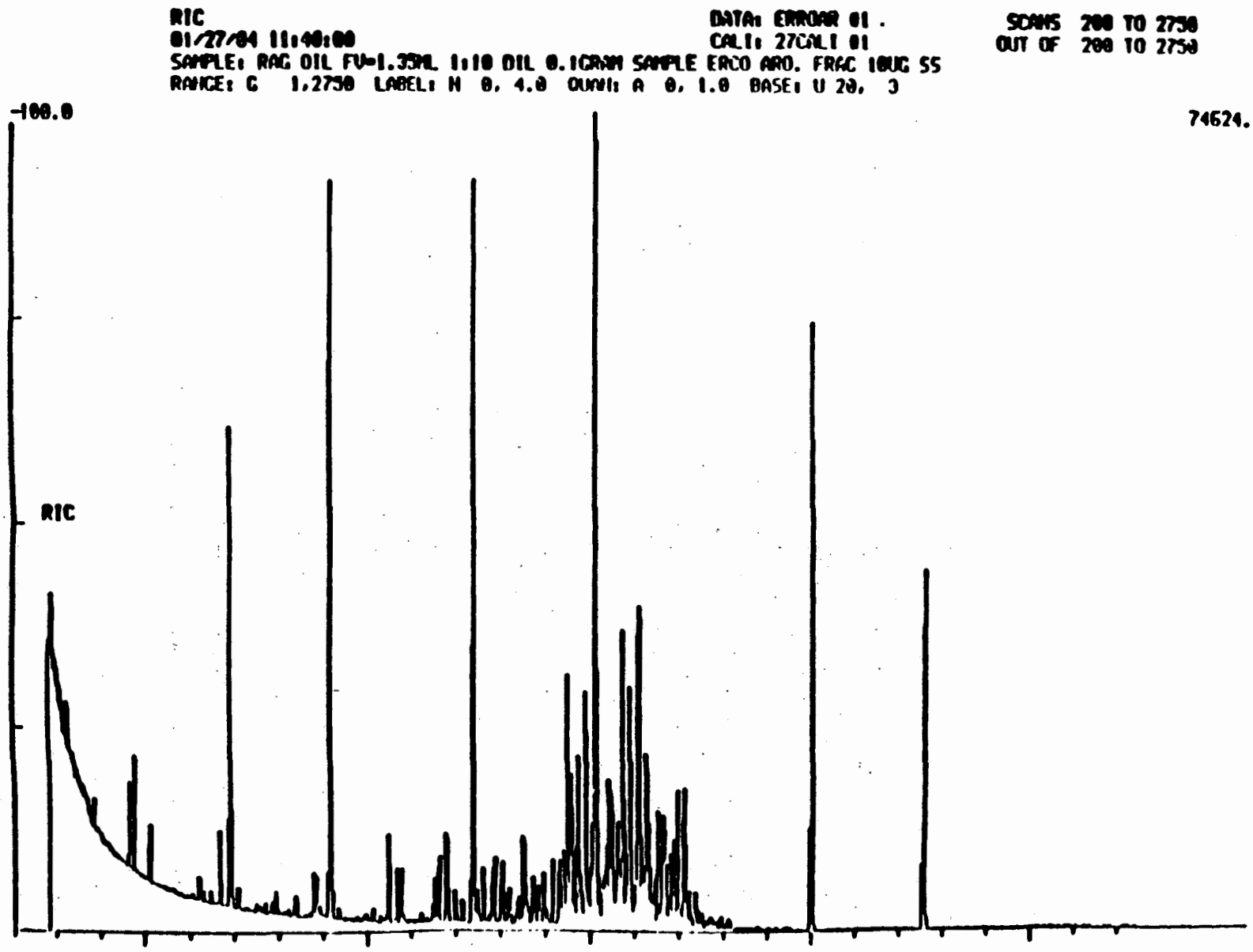


Figure 1. Reconstructed ion chromatogram from GC/MS analysis of the aromatic fraction from Rag Oil

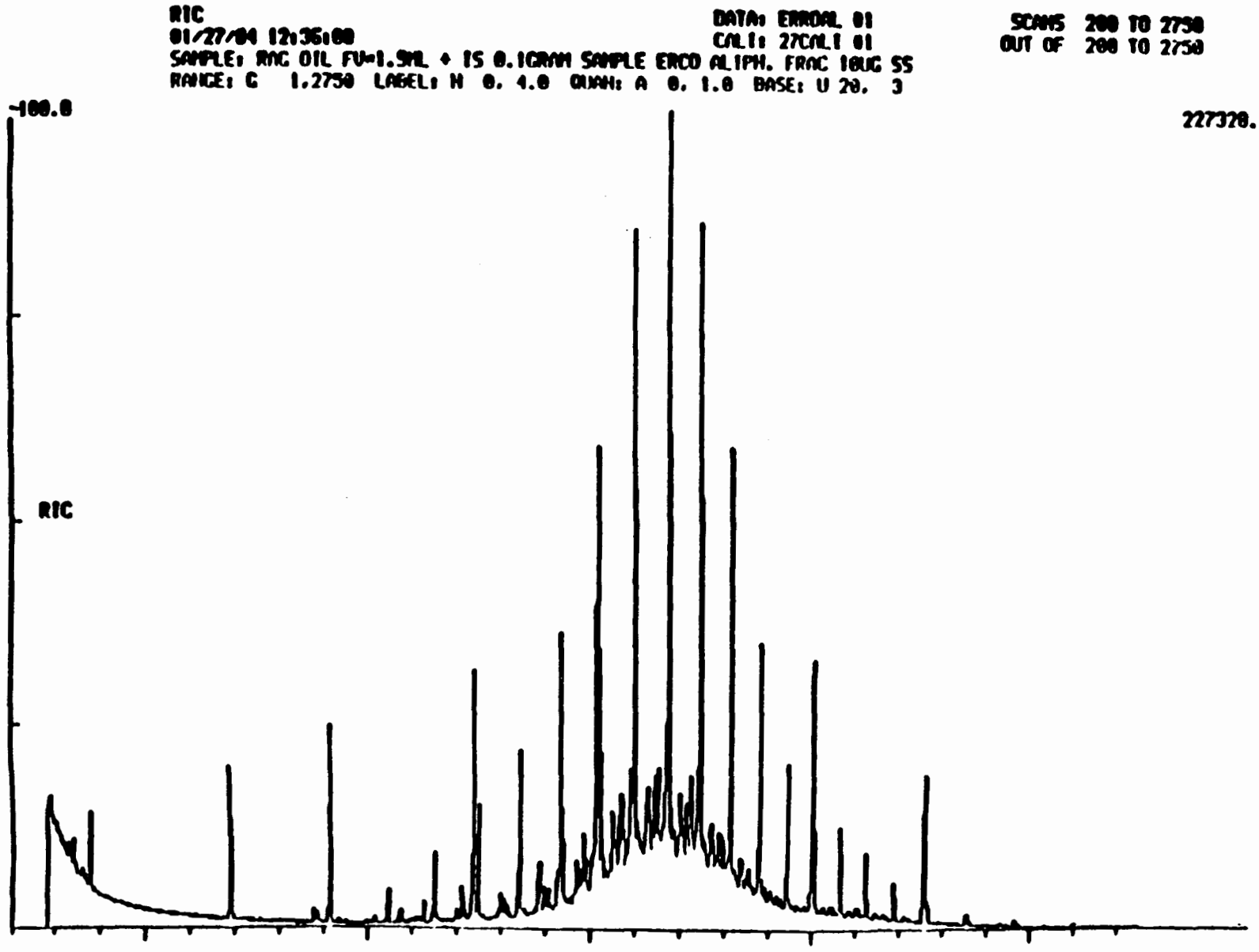
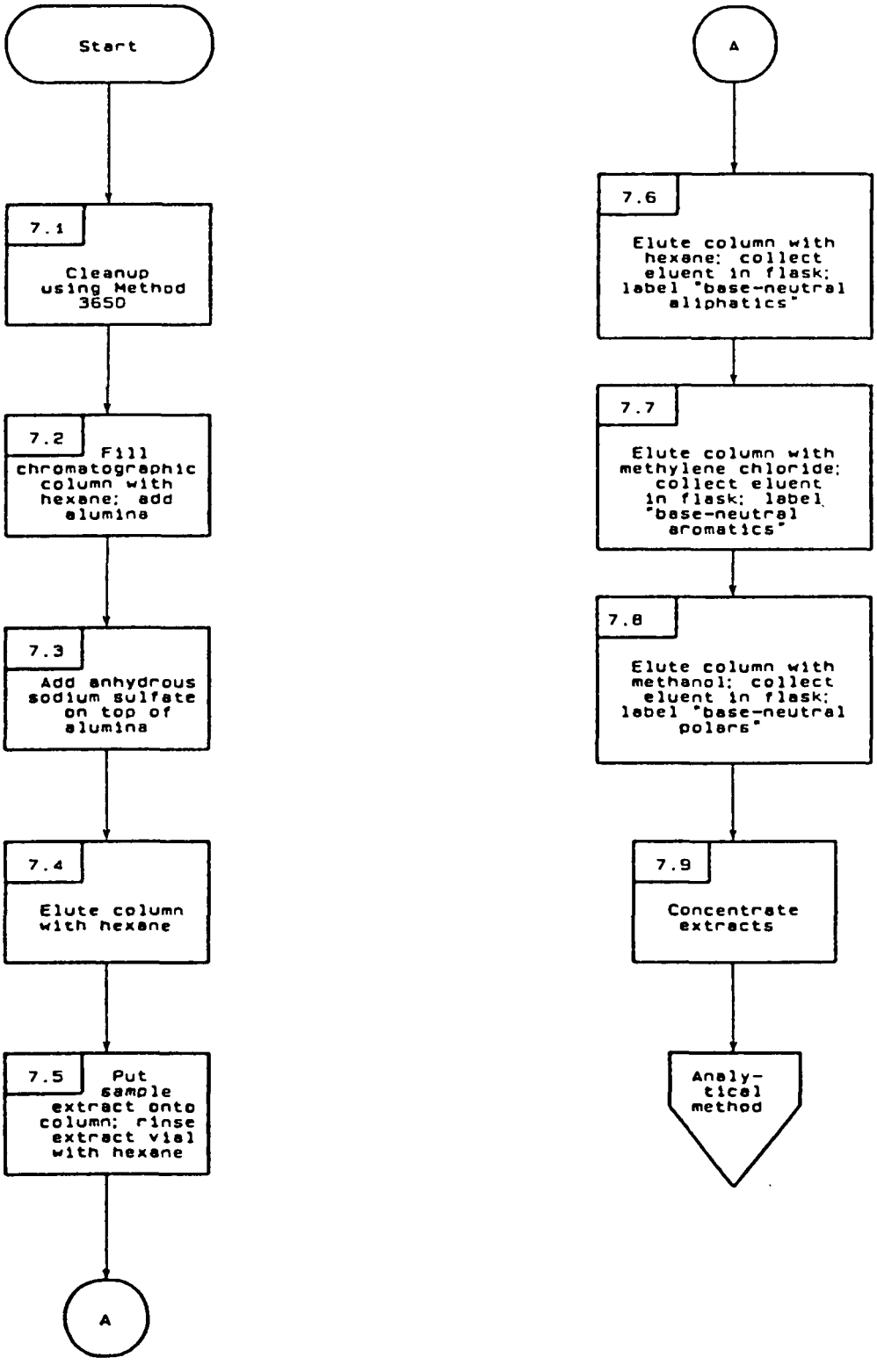


Figure 2. Reconstructed ion chromatogram from GC/MS analysis of the aliphatic fraction from Rag Oil

METHOD 3611

ALUMINA COLUMN CLEANUP AND SEPARATION OF PETROLEUM WASTES



Revision 0
Date September 1986

METHOD 3620

FLORISIL COLUMN CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Florisil, a registered tradename of the Floridin Co., is a magnesium silicate with acidic properties. It is used for general column chromatography as a cleanup procedure prior to sample analysis by gas chromatography.

1.2 General applications: Cleanup of pesticide residues and other chlorinated hydrocarbons; the separation of nitrogen compounds from hydrocarbons; the separation of aromatic compounds from aliphatic-aromatic mixtures; and similar applications for use with fats, oils, and waxes (Floridin). Additionally, Florisil is considered good for separations with steroids, esters, ketones, glycerides, alkaloids, and some carbohydrates (Gordon and Ford).

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing the following analyte groups: phthalate esters; nitrosamines; organochlorine pesticides; nitroaromatics; haloethers; chlorinated hydrocarbons; and organophosphorous pesticides.

2.0 SUMMARY OF METHOD

2.1 The column is packed with the required adsorbent, topped with a water adsorbent, and then loaded with the sample to be analyzed. Elution is effected with a suitable solvent(s) leaving the interfering compounds on the column. The eluate is then concentrated.

3.0 INTERFERENCES

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

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

4.0 APPARATUS AND MATERIALS

4.1 Beaker: 500-mL.

4.2 Chromatographic column: 300-mm long x 10-mm I.D. or 400-mm long x 20-mm I.D., to be specified in Paragraph 7.0; 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-570001-0500 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 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Florisil: Pesticide residue (PR) grade (60/100 mesh); purchase-activated at 1250°F (677°C), stored in glass containers with ground-glass stoppers or foil-lined screw caps.

5.1.1 **Deactivation of Florisil:** for cleanup of phthalate esters. To prepare for use, place 100 g of Florisil into a 500-mL beaker and heat for approximately 16 hr at 40°C. After heating, transfer to a 500-mL reagent bottle. Tightly seal and cool to room temperature. When cool add 3 mL of reagent water. Mix thoroughly by shaking or rolling for 10 min and let stand for at least 2 hr. Keep the bottle sealed tightly.

5.1.2 **Activation of Florisil:** for cleanup of nitrosamines, organochlorine pesticides and PCBs, nitroaromatics, haloethers, chlorinated hydrocarbons, and organophosphorous pesticides. Just before use, activate each batch at least 16 hr at 130°C in a glass container loosely covered with aluminum foil. Alternatively, store the Florisil in an oven at 130°C. Cool the Florisil before use in a desiccator.

(Florisil from different batches or sources may vary in adsorptive capacity. To standardize the amount of Florisil which is used, the use of lauric acid value is suggested. The referenced procedure determines the adsorption from hexane solution of lauric acid (mg) per g of Florisil. The amount of Florisil to be used for each column is calculated by dividing 110 by this ratio and multiplying by 20 g (Mills).)

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

5.3 Eluting solvents:

5.3.1 **Diethyl ether:** Pesticide quality or equivalent.

5.3.1.1 Must be free of peroxides as indicated by EM Quant test strips (available from EM Laboratories Inc., 500 Executive Boulevard, Elmsford, NY 10523).

5.3.1.2 Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethyl alcohol preservative must be added to each liter of ether.

5.3.2 **Acetone; hexane; methylene chloride; pentane; petroleum ether** (boiling range 30-60°C): 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 Phthalate esters:

7.1.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.1.2 Place 10 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top.

7.1.3 Preelute the column with 40 mL of hexane. The rate for all elutions should be about 2 mL/min. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 40 mL of hexane and continue the elution of the column. Discard this hexane eluate.

7.1.4 Next, elute the column with 100 mL of 20% ethyl ether in hexane (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction. No solvent exchange is necessary. Adjust the volume of the cleaned-up extract to whatever volume is required (10 mL for Method 8060) and analyze by gas chromatography. Compounds that elute in this fraction are:

Bis(2-ethylhexyl)phthalate
Butyl benzyl phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

7.2 Nitrosamines:

7.2.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.2.2 Place 22 g of activated Florisil into a 20-mm I.D. chromatographic column. Tap the column to settle the Florisil and add about 5 mm of anhydrous sodium sulfate to the top.

7.2.3 Preelute the column with 40 mL of ethyl ether/pentane (15:85) (v/v). Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the 2-mL sample extract onto the column using an additional 2 mL of pentane to complete the transfer.

7.2.4 Elute the column with 90 mL of ethyl ether/pentane (15:85) (v/v) and discard the eluate. This fraction will contain the diphenylamine, if it is present in the extract.

7.2.5 Next, elute the column with 100 mL of acetone/ethyl ether (5:95) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction will contain all of the nitrosamines listed in the scope of the method.

7.2.6 Add 15 mL of methanol to the collected fraction, concentrate using pentane to prewet the K-D column and set the water bath at 70 to 75°C. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of pentane. Analyze by gas chromatography.

7.3 Organochlorine pesticides, haloethers, and organophosphorous pesticides (see Tables 1 and 2 for fractionation patterns of compounds tested):

7.3.1 Reduce the sample extract volume to 10 mL prior to cleanup. The extract solvent must be hexane.

7.3.2 Add a weight of Florisil (nominally 20 g), predetermined by calibration, to a 20-mm I.D. chromatographic column. Settle the Florisil by tapping the column. Add anhydrous sodium sulfate to the top of the Florisil to form a layer 1 to 2 cm deep. Add 60 mL of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatographic column. Discard the eluate.

7.3.3 Adjust the sample extract volume to 10 mL with hexane and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 mL hexane, adding each rinse to the column.

7.3.4 Place a 500-mL K-D flask and clean concentrator tube under the chromatographic column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column with 200 mL of 6% ethyl ether in hexane (v/v) (Fraction 1) using a drip rate of about 5 mL/min. All of the haloethers are in this fraction. Remove the K-D flask and set aside for later concentration. Elute the column again, using 200 mL of 15% ethyl ether in hexane (v/v) (Fraction 2), into a second K-D flask. Perform a third elution using 200 mL of 50% ethyl ether in hexane (v/v) (Fraction 3), and a final elution with 200 mL of 100% ethyl ether (Fraction 4), into separate K-D flasks.

7.3.5 Concentrate the eluates by standard K-D techniques using the water bath at about 85°C (75°C for Fraction 4). Adjust the final volume to whatever volume is required (1-10 mL). Analyze by gas chromatography.

7.4 Nitroaromatics and isophorone:

7.4.1 Reduce the sample extract volume to 2 mL prior to cleanup.

7.4.2 Prepare a slurry of 10 g activated Florisil in methylene chloride/hexane (1:9) (v/v) and place the Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 cm of anhydrous sodium sulfate to the top. Adjust the elution rate to about 2 mL/min.

7.4.3 Just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract onto the column using an additional 2 mL of hexane to complete the transfer. Just prior to exposure of the sodium sulfate layer to the air, add 30 mL of methylene chloride/hexane (1:9) (v/v) and continue the elution of the column. Discard the eluate.

7.4.4 Next, elute the column with 30 mL of acetone/methylene chloride (1:9) (v/v) into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Concentrate the collected fraction, while exchanging the solvent to hexane. To exchange the solvent, reduce the elution solvent to about 10 mL. Add 50 mL of hexane, a fresh boiling chip, and return the reassembled K-D apparatus to the hot water bath. Adjust the

TABLE 1

DISTRIBUTION OF CHLORINATED PESTICIDES, PCBs, AND HALOETHERS INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]		
	1	2	3
Aldrin	100		
α-BHC	100		
β-BHC	97		
δ-BHC	98		
γ-BHC	100		
Chlordane	100		
4,4'-DDD	99		
4,4'-DDE	98		
4,4'-DDT	100		
Dieldrin	0	100	
Endosulfan I	37	64	
Ensosulfan II	0	7	91
Endosulfan sulfate	0	0	106
Endrin	4	96	
Endrin aldehyde	0	68	26
Haloethers	R		
Heptachlor	100		
Heptachlor epoxide	100		
Toxaphene	96		
PCB-1016	97		
PCB-1221	97		
PCB-1232	95	4	
PCB-1242	97		
PCB-1248	103		
PCB-1254	90		
PCB-1260	95		

[a]Eluant composition: Fraction 1 - 6% ethyl ether in hexane
Fraction 2 - 15% ethyl ether in hexane
Fraction 3 - 50% ethyl ether in hexane

R = Recovered (no percent recovery data presented).

SOURCE: U.S. EPA and FDA data.

TABLE 2

DISTRIBUTION OF ORGANOPHOSPHOROUS PESTICIDES
INTO FLORISIL COLUMN FRACTIONS

Parameter	Percent Recovery by Fraction[a]			
	1	2	3	4
Azinophos methyl			20	80
Bolstar (Sulprofos)	ND	ND	ND	ND
Chlorpyrifos	>80			
Coumaphos	NR	NR	NR	
Demeton	100			
Diazinon		100		
Dichlorvos	NR	NR	NR	
Dimethoate	ND	ND	ND	ND
Disulfoton	25-40			
EPN		>80		
Ethoprop	V	V	V	
Fensulfothion	ND	ND	ND	ND
Fenthion	R	R		
Malathion		5	95	
Merphos	V	V	V	
Mevinphos	ND	ND	ND	ND
Monochrotophos	ND	ND	ND	ND
Naled	NR	NR	NR	
Parathion		100		
Parathion methyl		100		
Phorate	0-62			
Ronnel	>80			
Stirophos (Tetrachlorvinphos)	ND	ND	ND	ND
Sulfotepp	V	V		
TEPP	ND	ND	ND	ND
Tokuthion (Prothiofos)	>80			
Trichloronate	>80			

[a]Eluant composition: Fraction 1 - 200 mL of 6% ethyl ether in hexane
Fraction 2 - 200 mL of 15% ethyl ether in hexane
Fraction 3 - 200 mL of 50% ethyl ether in hexane
Fraction 4 - 200 mL of 100% ethyl ether

R = Recovered (no percent recovery information presented) (U.S. FDA).
NR = Not recovered (U.S. FDA).
V = Variable recovery (U.S. FDA).
ND = Not determined.

SOURCE: U.S. EPA and FDA data.

final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Compounds that elute in this fraction are:

2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Nitrobenzene.

Analyze by gas chromatography.

7.5 Chlorinated hydrocarbons:

7.5.1 Reduce the sample extract volume to 2 mL prior to cleanup. The extract solvent must be hexane.

7.5.2 Place 12 g of Florisil into a 10-mm I.D. chromatographic column. Tap the column to settle the Florisil and add 1 to 2 cm of anhydrous sodium sulfate to the top.

7.5.3 Preelute the column with 100 mL of petroleum ether. Discard the eluate and, just prior to exposure of the sodium sulfate layer to the air, quantitatively transfer the sample extract to the column by decantation and subsequent petroleum ether washings. Discard the eluate. Just prior to exposure of the sodium sulfate layer to the air, begin eluting the column with 200 mL of petroleum ether and collect the eluate in a 500-mL K-D flask equipped with a 10-mL concentrator tube. This fraction should contain all of the chlorinated hydrocarbons:

2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
1,2,4-Trichlorobenzene.

7.5.4 Concentrate the fraction, using hexane to prewet the column. When the apparatus is cool, remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with hexane. Adjust the final volume of the cleaned-up extract to whatever volume is required (1-10 mL). Analyze by gas chromatography.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds 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 should also be processed through this cleanup method.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the distribution of chlorinated pesticides, PCB's, and haloethers in various Florisil column fractions.

9.2 Table 2 indicates the distribution of organophosphorous pesticides in various Florisil column fractions.

10.0 REFERENCES

1. Gordon, A.J. and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. Floridin of ITT System, Florisil: Properties, Application, Bibliography, Pittsburgh, Pennsylvania, 5M381DW.

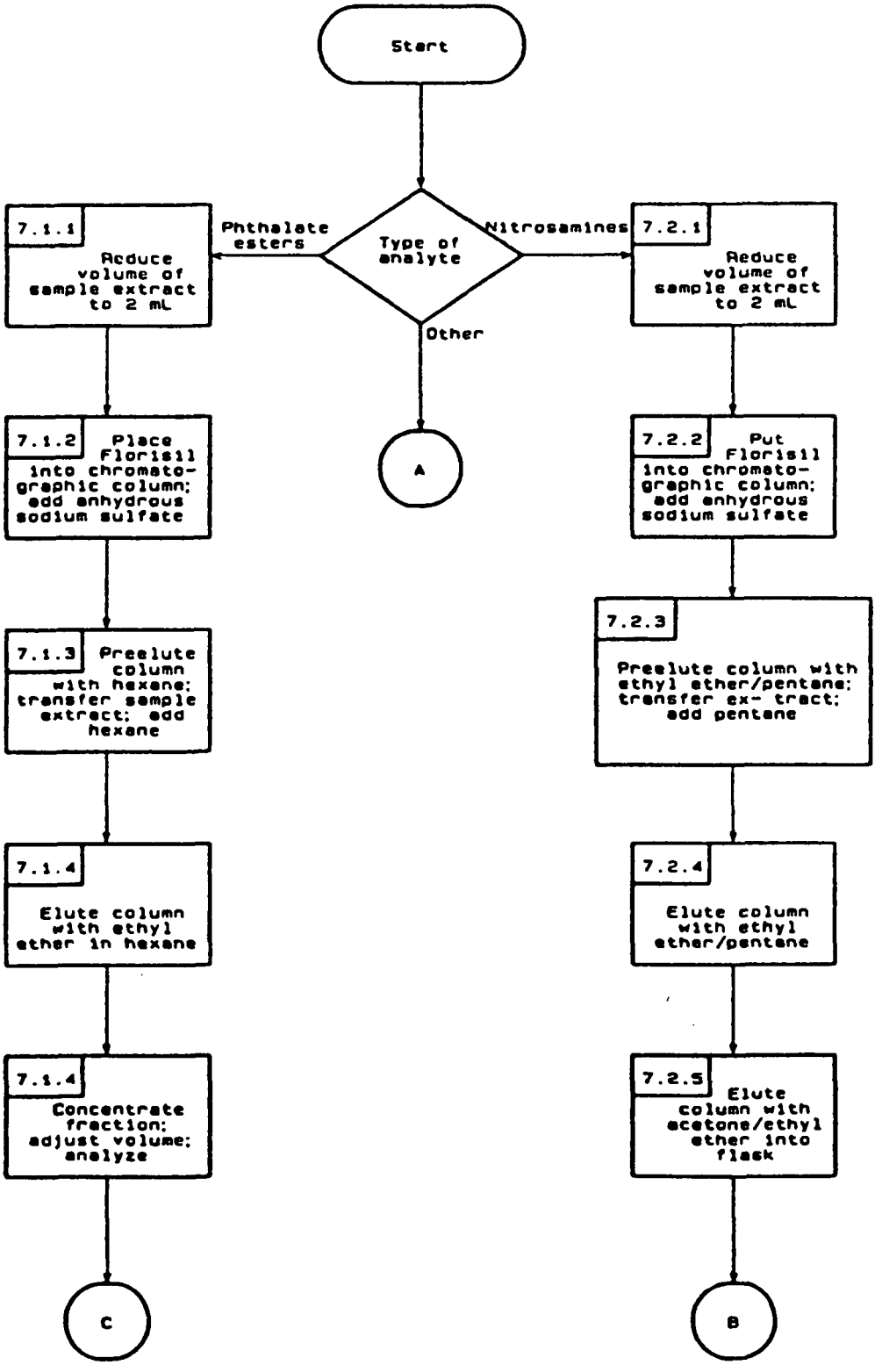
3. Mills, P.A., "Variation of Florisil Activity; Simple Method for Measuring Absorbent Capacity and its use in Standardizing Florisil Columns," Journal of the Association of Official Analytical Chemists, 51, 29, 1968.

4. U.S. Food and Drug Association, Pesticides Analytical Manual (Volume 1), July 1985.

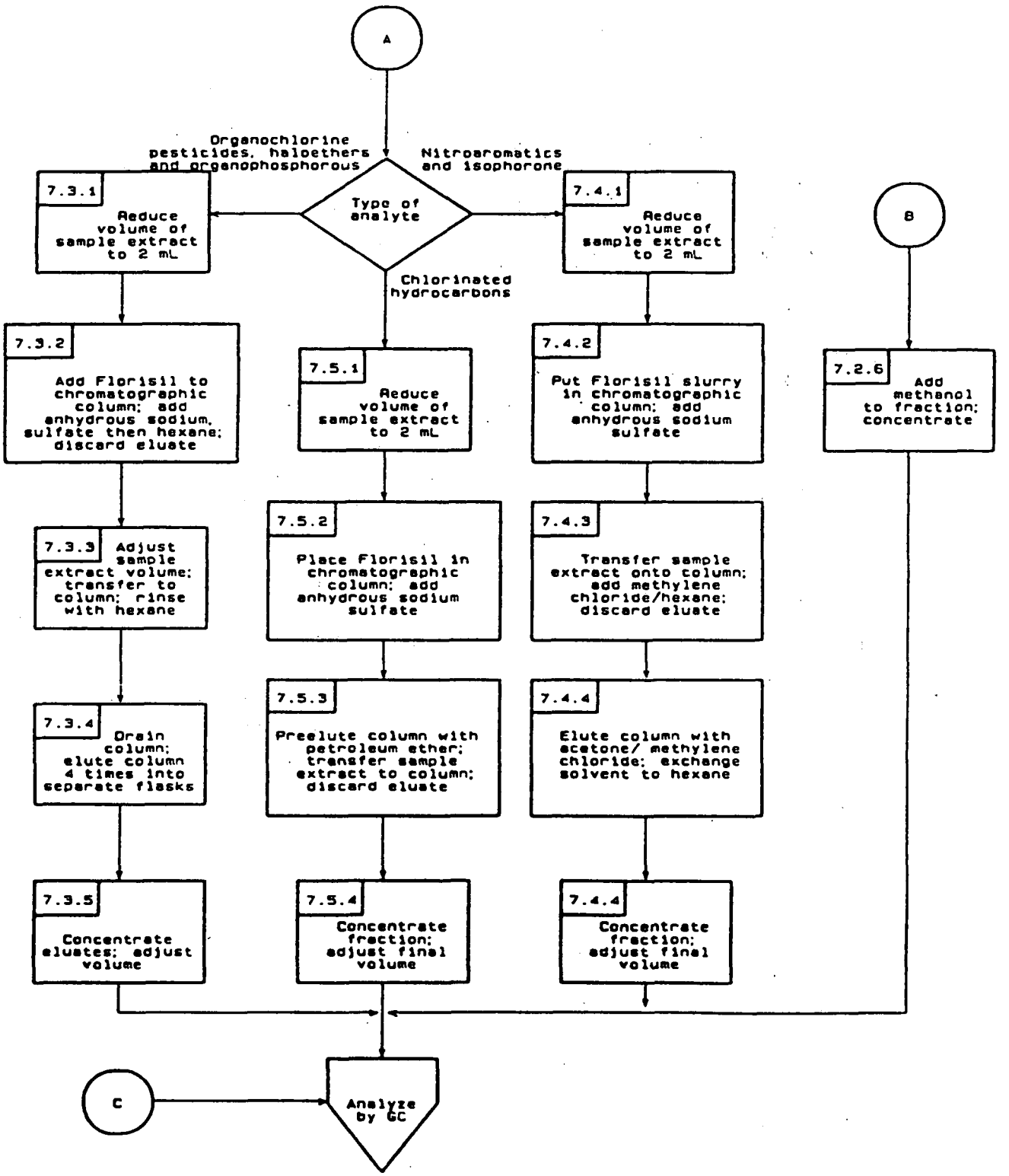
5. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

METHOD 3620

FLORISIL COLUMN CLEANUP



FLORISIL COLUMN CLEANUP
(Continued)



METHOD 3630

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 for column chromatography and is for separating the analytes from interfering compounds of a different chemical polarity.

1.2 General applications (Gordon and Ford):

1.2.1 **Activated:** Heated at 150-160°C for several hours. USES: Separation of hydrocarbons.

1.2.2 **Deactivated:** Containing 10-20% water. USES: An adsorbent for most functionalities with ionic or nonionic characteristics, including alkaloids, sugar esters, glycosides, dyes, alkali metal cations, lipids, glycerides, steroids, terpenoids and plasticizers. The disadvantages of deactivated silica gel are that the solvents methanol and ethanol decrease adsorbent activity.

1.3 Specific applications: This method includes guidance for cleanup of sample extracts containing polynuclear aromatic hydrocarbons and derivatized phenolic compounds.

2.0 SUMMARY OF METHOD

2.1 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.

3.0 INTERFERENCES

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

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

4.0 APPARATUS AND MATERIALS

4.1 Chromatographic column: 250-mm long x 10-mm I.D.; 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 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-570001-0500 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 Muffle furnace.

4.5 Reagent bottle: 500-mL.

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.8 Erlenmeyer flasks: 50- and 250-mL.

5.0 REAGENTS

5.1 Silica gel: 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.

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

5.3 Eluting solvents: Cyclohexane, hexane, 2-propanol, toluene, methylene chloride, pentane (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 Polynuclear aromatic hydrocarbons:

7.1.1 Before the silica gel cleanup technique can be utilized, the extract solvent must be exchanged to cyclohexane. Add 1 to 10 mL of the sample extract (in methylene chloride) and a boiling chip to a clean K-D concentrator tube. Add 4 mL of cyclohexane and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of methylene chloride to the top. Place the micro-K-D apparatus on a boiling (100°C) water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the micro-Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the extract volume to about 2 mL.

7.1.2 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10-mm I.D. 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.

7.1.3 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.

7.1.4 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 or GC analysis. Components that elute in this fraction are:

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Benzo(ghi)perylene
Benzo(k)fluoranthene
Chrysene
Dibenzo(a,h)anthracene
Fluoranthene
Fluorene

Indeno(1,2,3-cd)pyrene
Naphthalene
Phenanthrene
Pyrene

7.2 Derivatized phenols:

7.2.1 This silica gel cleanup procedure is performed on sample extracts that have undergone pentafluorobenzyl bromide derivatization as described in Method 8040.

7.2.2 Place 4.0 g of activated silica gel into a 10-mm I.D. 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.

7.2.3 Preelute 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.

7.2.4 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).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds 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 Table 1 provides performance information on the fractionation of phenolic derivatives using this method.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References, (New York: John Wiley & Sons, Inc.), pp. 372, 374, and 375, 1972.

2. 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. SILICA GEL FRACTIONATION OF PFBB DERIVATIVES

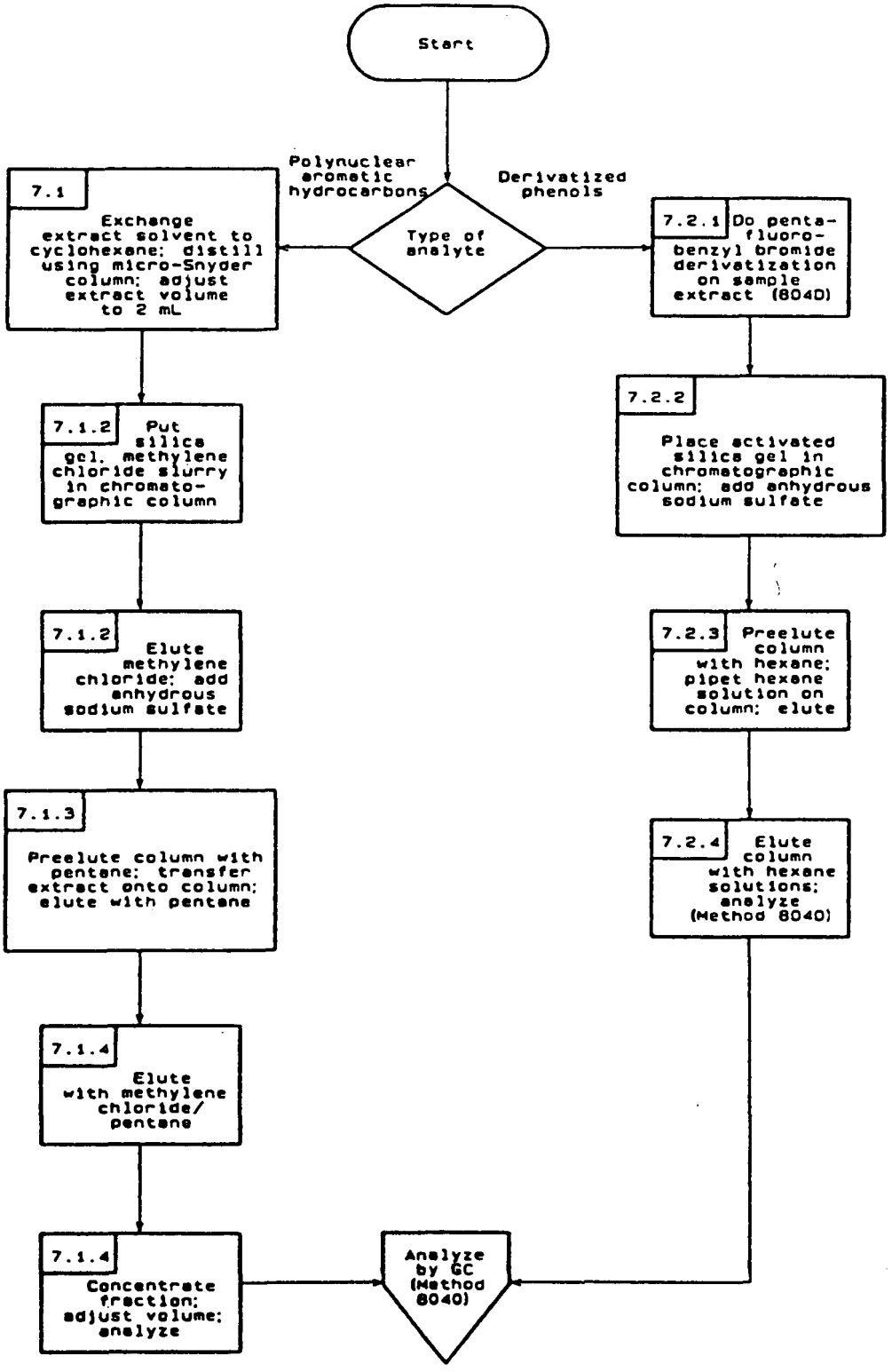
Parameter	Percent Recovery by Fraction[1]			
	1	2	3	4
2-Chlorophenol		90	1	
2-Nitrophenol			9	90
Phenol		90	10	
2,4-Dimethylphenol		95	7	
2,4-Dichlorophenol		95	1	
2,4,6-Trichlorophenol	50	50		
4-Chloro-3-methylphenol		84	14	
Pentachlorophenol	75	20		
4-Nitrophenol			1	90

[1] 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.

METHOD 3630

SILICA GEL CLEANUP



METHOD 3640

GEL-PERMEATION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Gel-permeation chromatography (GPC) is a size exclusion procedure using organic solvents and hydrophobic gels in the separation of synthetic macromolecules (Gordon and Ford). 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 greater than those of the molecules to be separated (Shugar, et al.).

1.2 General 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 (Shugar, et al.).

1.3 Specific application: This method includes guidance for cleanup of sample extracts containing the compounds listed in Tables 2-1 through 2-9 of Chapter 2.

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 to be analyzed. 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 method detection limit before this method is performed on actual samples.

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

4.0 APPARATUS

4.1 Gel permeation chromatography system: (Analytical Biochemical Laboratories, Inc. GPC autoprep Model 1002A or equivalent). An automated system of this type is not required; however, if not used, equivalency of an alternative system must be shown.

4.1.1 **Chromatographic column:** 600- to 700-mm x 25-mm I.D. glass column fitted for upward flow operation.

4.1.2 **Bio-beads S-X3:** 70 g per column.

4.1.3 **Pump:** Capable of constant flow of 0.1 to 5 mL/min at up to 100 psi.

4.1.4 **Injector:** With 5-mL loop.

4.1.5 **Ultraviolet detector:** 254-nm (optional).

4.1.6 **Strip-chart recorder:** (optional).

4.1.7 **Syringe:** 10-mL with Luerlok fitting.

4.1.8 **Syringe filter holder and filter:** BioRad "Prep Disc" sample filter # 343-0005 and 5-um size filters or equivalent.

4.2 Beakers: 400-mL.

5.0 REAGENTS

5.1 Methylene chloride: Pesticide quality or equivalent.

5.2 GPC calibration solutions:

5.2.1 **Corn oil:** 200 mg/mL in methylene chloride.

5.2.2 **Bis(2-ethylhexyl)phthalate and pentachlorophenol solution:** 4.0 mg/mL in methylene chloride.

5.2.3 Mix the corn oil with the phthalate/phenol solution if a UV detector is used. The concentrations should remain the same.

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 Packing the column: Place approximately 70 g of Bio Beads SX-3 in a 400-mL beaker. Cover the beads with methylene chloride; allow the beads to swell overnight (before packing the columns). Transfer the swelled beads to the column and start pumping solvent through the column, from bottom to top, at 5.0 mL/min. After approximately 1 hr, adjust the pressure on the column to 7-10 psi and pump an additional 4 hr to remove air from the column. Adjust the column pressure periodically as required to maintain 7-10 psi. (See the instrument manual for more details on packing the column.) The pressure should not be permitted to exceed 25 psi.

7.2 Calibration of the column: The column can either be calibrated manually by gravimetric/GC/FID techniques or automatically if a recording UV detector with a flow through cell is available.

7.2.1 **Manual calibration:** Load 5 mL of the corn oil solution into sample loop No. 1 and 5 mL of the phthalate-phenol solution into loop No. 2. Inject the corn oil and collect 10-mL fractions (i.e., change fractions at 2-min intervals) for 36 min. Inject the phthalate-phenol solution and collect 15 mL fractions for 60 min. Determine the corn oil elution pattern by evaporation of each fraction to dryness followed by a gravimetric determination of the residue. Analyze the phthalate-phenol fractions by GC/FID using a DB-5 capillary column, a UV spectrophotometer, or a GC/MS system. Plot the concentration of each component in each fraction versus total eluant volume (or time) from the injection points. Choose a dump time which allows $\geq$ 85% removal of the corn oil and $\geq$ 85% recovery of the bis(2-ethylhexyl)phthalate. Choose the collect time to extend at least 10 min after the elution of pentachlorophenol. Wash the column with methylene chloride at least 15 min between samples. Typical parameters selected are: Dump time, 30 min (150 mL); collect time, 36 min (180 mL); and wash time, 15 min (75 mL).

7.2.2 **Automated calibration:** The column can also be calibrated by the use of a 254-nm detector in place of gravimetric and GC analyses of fractions. Use the corn oil/phthalate/phenol mixture when using a UV detector. Load 5 mL into sample loop No. 1. Use the same criteria for choosing dump time and collect time as in the manual calibration.

7.2.3 The SX-3 Bio Beads column may be reused for several months, even if discoloration occurs. Recalibrate the system once a week.

7.3 GPC Extract Cleanup: The extract must be in methylene chloride or, primarily methylene chloride. All other solvents must be concentrated to 1 mL and diluted to 10.0 mL with methylene chloride. Prefilter or load all extracts via the filter holder to avoid particulates that might cause flow stoppage or damage the valve. Load one 5.0 mL aliquot of the extract onto the GPC column. Do not apply excessive pressure when loading. Purge the sample loading tubing thoroughly with solvent between extracts. After especially dirty extracts, run a GPC blank (methylene chloride) to check for carry-over. Process the extracts using the dump, collect, and wash parameters determined from the calibration, and collect the cleaned extracts in 400-mL beakers tightly covered with aluminum foil.

NOTE: Half of the 10.0 mL extract is lost during the loading of the GPC. Therefore, divide the sample size by two when calculating analyte concentration.

7.4 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 required final volume.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedure.

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

8.2 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 the determinative methods for performance data.

10.0 REFERENCES

1. Gordon, A.J., and R.A. Ford, The Chemist's Companion: A Handbook of Practical Data, Techniques, and References (New York: John Wiley & Sons, Inc.) pp. 372, 374, and 375, 1972.

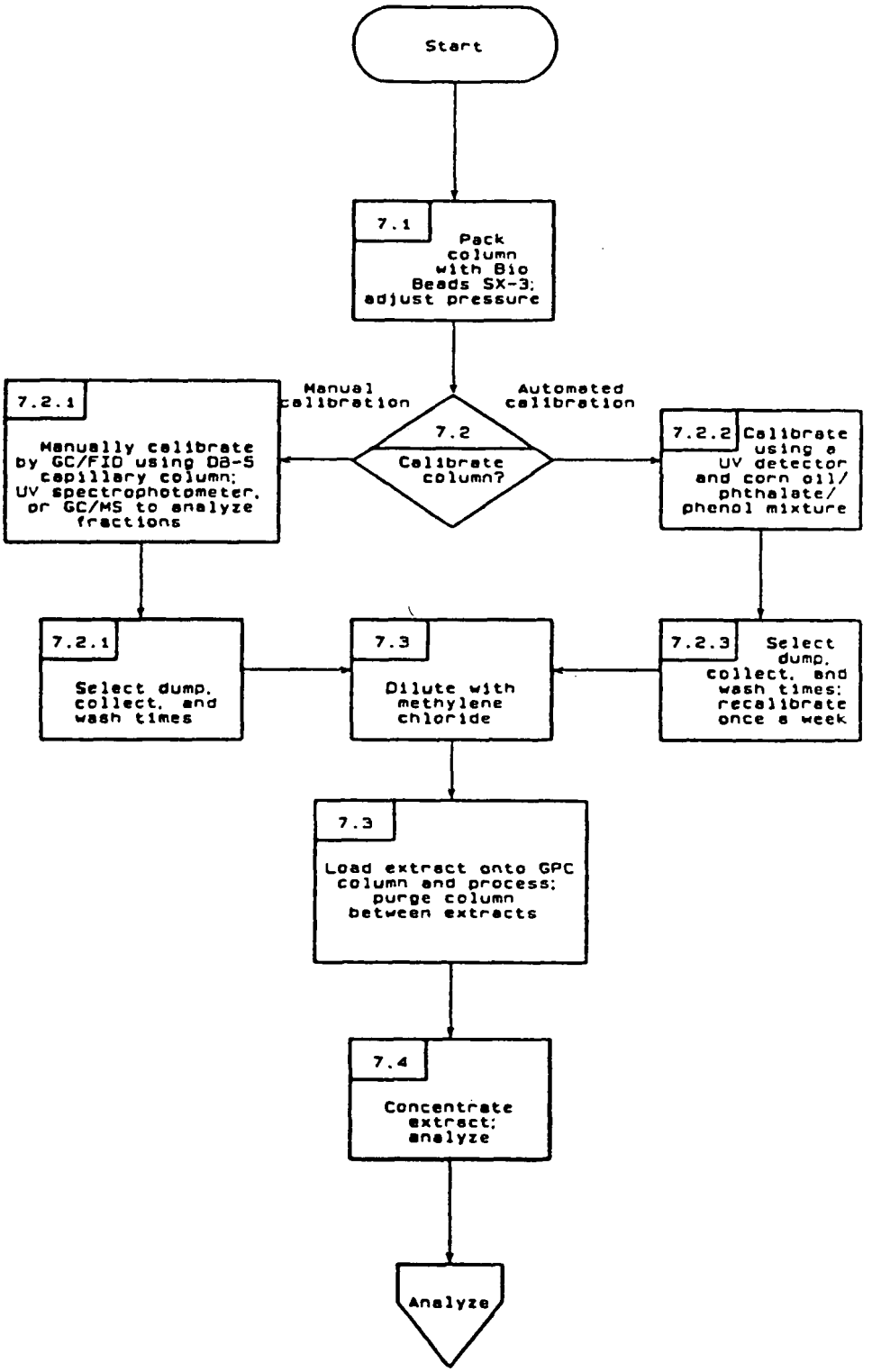
2. Shugar G.J., et al., Chemical Technician's Ready Reference Handbook, 2nd ed. (New York: McGraw-Hill Book Co.) pp. 764-766, 1981.

3. Wise, R.H., D.F. Bishop, R.T. Williams, and B.M. Austern, "Gel Permeation Chromatography in the GC/MS Analysis of Organics in Sludges," U.S. EPA, Municipal Environmental Research Laboratory, Cincinnati, Ohio 45268.

4. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

METHOD 3640

GEL-PERMEATION CLEANUP



Revision 0
Date September 1986

METHOD 3650

ACID-BASE PARTITION CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Method 3650 was formally Method 3530 in the second edition of this manual.

1.2 This is a liquid-liquid partitioning method to separate acid analytes from base/neutral analytes using pH adjustment. It may be used for cleanup of petroleum waste prior to alumina cleanup.

2.0 SUMMARY OF METHOD

2.1 The solvent extract 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 ready for further cleanup, if necessary, or analysis. The aqueous layer is acidified and extracted with an organic solvent. This extract is concentrated and then ready for analysis for the acid analytes.

3.0 INTERFERENCES

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

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

4.0 APPARATUS AND MATERIALS

4.1 Separatory funnel: 125-mL, 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 K5700-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts.

4.3.2 **Evaporation flask:** 500-mL (K-570001-0500 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 K569001-0219 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 (±5°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: 125-mL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Sodium hydroxide solution 10N: (ACS) 40 g NaOH in reagent water and dilute to 100 mL.

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

5.4 Sulfuric acid solution (1:1): Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.5 Solvents: Acetone, methanol, ethyl ether, methylene chloride (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 Place 10 mL of the extract or organic liquid waste to be cleaned up into the separatory funnel.

7.2 Add 20 mL of methylene chloride to the separatory funnel.

7.3 Add 20 mL of reagent water and adjust the pH to 12-13 with sodium hydroxide.

7.4 Seal and shake the separatory funnel for 1-2 min 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 min. If the emulsion interface between layers is more than one-third of 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 portions of reagent water pH 12-13. Combine the aqueous extracts.

7.7 At this point the analytes will be in the organic and/or in the aqueous phase. Organic acids and phenols will be in the aqueous phase, whereas, base/neutral analytes will be in the organic solvent. If the analytes are in the aqueous phase only, discard the organic phase and proceed to Paragraph 7.8. If the analytes are in the organic phase, discard the aqueous phase and proceed to Paragraph 7.10.

7.8 Transfer the aqueous phase to a clean separatory funnel. Adjust the aqueous layer to a pH of 1-2 with sulfuric acid. Add 20 mL of methylene chloride to the separatory funnel and shake for 2 min. Allow the solvent to separate from the aqueous phase and collect the solvent in an Erlenmeyer flask.

7.9 Add a second 20 mL volume of methylene chloride to the separatory funnel and re-extract at pH 1-2 a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

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 the extracts by passing them through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Rinse the Erlenmeyer flask which contained the solvent extract and the column with 20 mL of methylene chloride to complete the quantitative transfer.

7.12 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 (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent.

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 (95°-100°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter but the chambers will not flood. When the apparent volume of the liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain for at least 10 min while cooling. Remove the 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 mL with solvent.

7.14 The acid fraction is now ready for analysis. If the base/neutral extract is to undergo further cleanup by the Alumina Column Cleanup for Petroleum Waste (Method 3611), the extract must be exchanged to hexane. To the 1-mL base/neutral extract, 5 mL of hexane should be added (solvent exchanged), and this mixture then reconcentrated to 1 mL using the micro-KD apparatus. 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 specific quality control procedures and Method 3600 for cleanup procedures.

8.2 The analyst should demonstrate that the compounds 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 be processed through this cleanup method.

9.0 METHOD PERFORMANCE

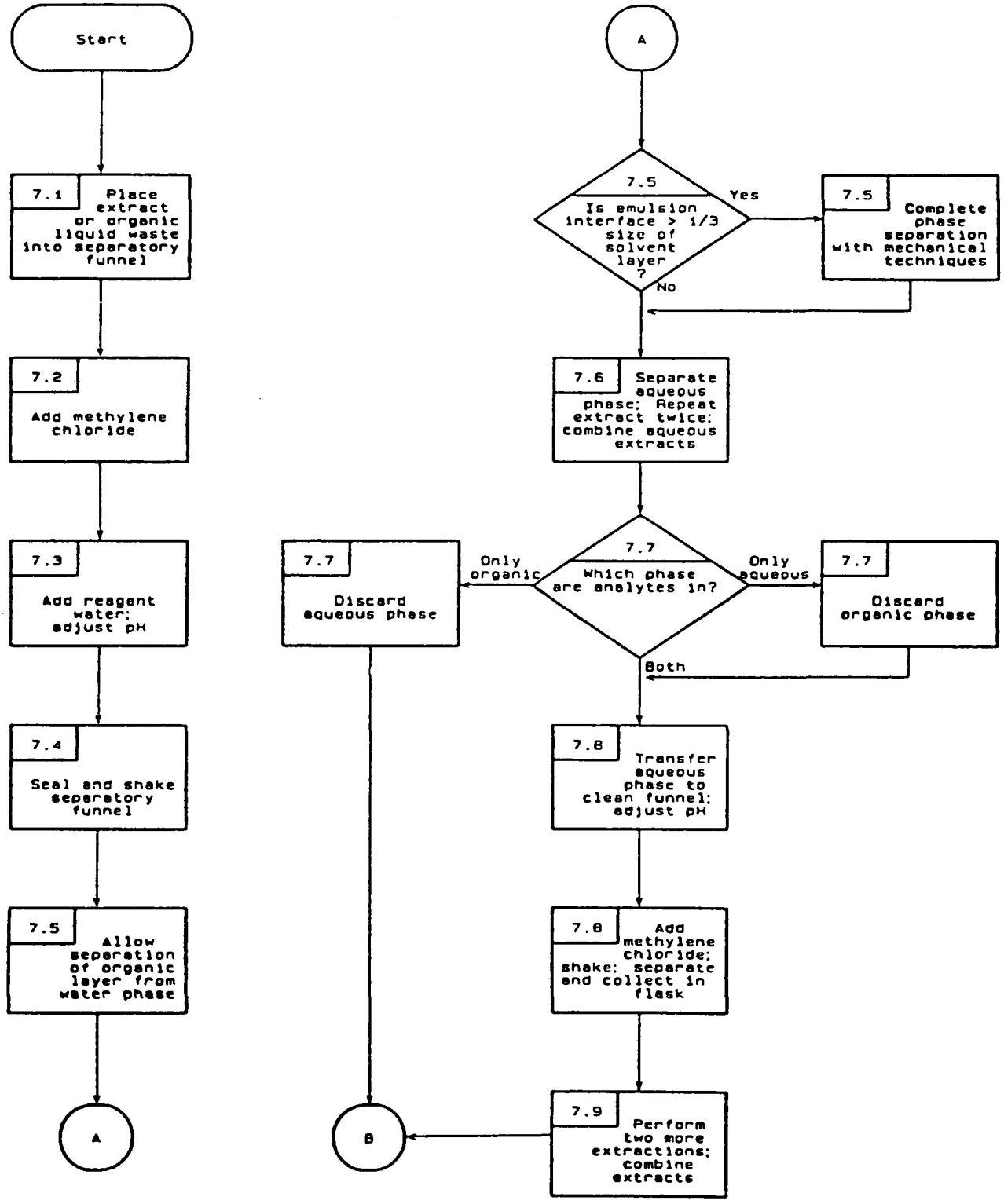
9.1 Refer to the determinative methods for performance data.

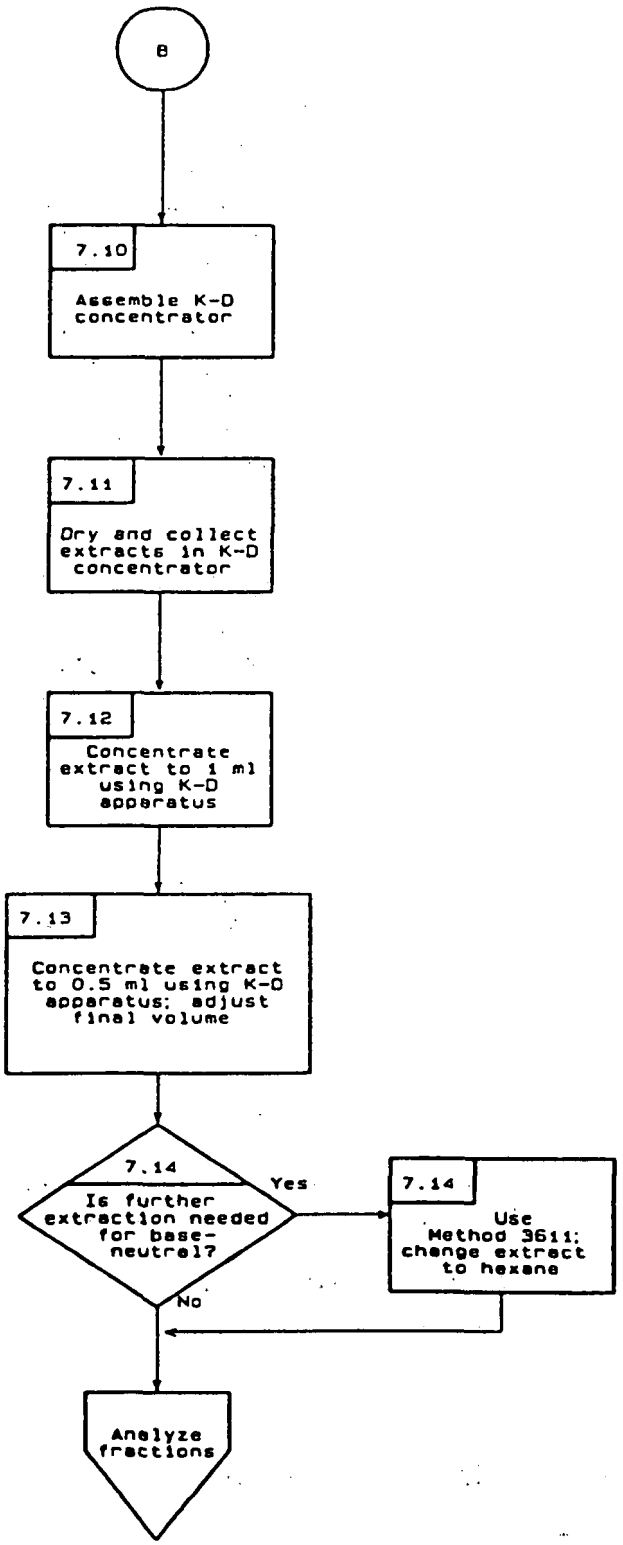
10.0 REFERENCES

10.1 None required.

METHOD 3650

ACID-BASE PARTITION CLEANUP




B
7.10
Assemble K-D concentrator
7.11
Dry and collect extracts in K-D concentrator
7.12
Concentrate extract to 1 ml using K-D apparatus
7.13
Concentrate extract to 0.5 ml using K-D apparatus; adjust final volume
7.14
Is further extraction needed for base-neutral?
Yes
No
7.14
Use Method 3611; change extract to hexane
Analyze fractions

METHOD 3660

SULFUR CLEANUP

1.0 SCOPE AND APPLICATION

1.1 Elemental sulfur is encountered in many sediment samples (generally specific to different areas in the country), marine algae, and some industrial wastes. The solubility of sulfur in various solvents is very similar to the organochlorine and organophosphorous pesticides; therefore, the sulfur interference follows along with the pesticides through the normal extraction and cleanup techniques. In general, sulfur will usually elute entirely in Fraction 1 of the Florisil cleanup (Method 3620).

1.2 Sulfur will be quite evident in gas chromatograms obtained from electron capture detectors, flame photometric detectors operated in the sulfur or phosphorous mode, and Coulson electrolytic conductivity detectors in the sulfur mode. If the gas chromatograph is operated at the normal conditions for pesticide analysis, the sulfur interference can completely mask the region from the solvent peak through Aldrin.

1.3 Three techniques for the elimination of sulfur are detailed within this method: (1) the use of copper powder; (2) the use of mercury; and (3) the use of tetrabutylammonium-sulfite. Tetrabutylammonium-sulfite causes the least amount of degradation of a broad range of pesticides and organic compounds, while copper and mercury may degrade organophosporous and some organochlorine pesticides.

2.0 SUMMARY OF METHOD

2.1 The sample to undergo cleanup is mixed with either copper, mercury, or tetrabutylammonium (TBA)-sulfite. The mixture is shaken and the extract is removed from the sulfur cleanup reagent.

3.0 INTERFERENCES

3.1 Removal of sulfur using copper:

3.1.1 The copper must be very reactive; therefore, all oxides of copper must be removed so that the copper has a shiny, bright appearance.

3.1.2 The sample extract must be vigorously agitated with the reactive copper for at least one minute.

4.0 APPARATUS AND MATERIALS

4.1 Mechanical shaker or mixer: Such as the Vortex Genie.

4.2 Pipets: Disposable, Pasteur type.

4.3 Centrifuge tubes: Calibrated, 12-mL.

4.4 Glass bottles or vials: 10-mL and 50-mL, with Teflon-lined screw-caps.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Nitric acid: Dilute.

5.3 Acetone, hexane, 2-propanol: Pesticide quality or equivalent.

5.4 Copper powder: Remove oxides by treating with dilute nitric acid, rinse with distilled water to remove all traces of acid, rinse with acetone and dry under a stream of nitrogen. (Copper, fine granular Mallinckrodt 4649 or equivalent).

5.5 Mercury: Triple distilled.

5.6 Tetrabutylammonium (TBA)-sulfite reagent: Dissolve 3.39 g tetrabutylammonium hydrogen sulfate in 100 mL reagent water. To remove impurities, extract this solution three times with 20-mL portions of hexane. Discard the hexane extracts, and add 25 g sodium sulfite to the water solution. Store the resulting solution, which is saturated with sodium sulfite, in an amber bottle with a Teflon-lined screw-cap. This solution can be stored at room temperature for at least one month.

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 Removal of sulfur using copper:

7.1.1 Concentrate the sample to exactly 1.0-mL in the Kuderna-Danish tube.

7.1.2 If the sulfur concentration is such that crystallization occurs, centrifuge to settle the crystals, and carefully draw off the sample extract with a disposable pipet leaving the excess sulfur in the K-D tube. Transfer the extract to a calibrated centrifuge tube.

7.1.3 Add approximately 2 g of cleaned copper powder (to the 0.5 mL mark) to the centrifuge tube. Mix for at least 1 min on the mechanical shaker.

7.1.4 Separate the extract from the copper by drawing off the extract with a disposable pipet and transfer to a clean vial. The volume remaining still represents 1.0 mL of extract.

NOTE: This separation is necessary to prevent further degradation of the pesticides.

7.2 Removal of sulfur using mercury:

NOTE: Mercury is a highly toxic metal and therefore, must be used with great care. Prior to using mercury, it is recommended that the analyst become acquainted with proper handling and cleanup techniques associated with this metal.

7.2.1 Concentrate the sample extract to exactly 1.0 mL.

7.2.2 Pipet 1.0 mL of the extract into a clean concentrator tube or Teflon-sealed vial.

7.2.3 Add one to three drops of mercury to the vial and seal. Agitate the contents of the vial for 15-30 sec. Prolonged shaking (2 hr) may be required. If so, use a mechanical shaker.

7.2.4 Separate the sample from the mercury by drawing off the extract with a disposable pipet and transfer to a clean vial.

7.3 Removal of sulfur using TBA-sulfite:

7.3.1 Concentrate the sample extract to exactly 1.0 mL.

7.3.2 Transfer the 1.0 mL to a 50-mL clear glass bottle or vial with a Teflon-lined screw-cap. Rinse the concentrator tube with 1 mL of hexane, adding the rinsings to the 50-mL bottle.

7.3.3 Add 1.0 mL TBA-sulfite reagent and 2 mL 2-propanol, cap the bottle, and shake for at least 1 min. If the sample is colorless or if the initial color is unchanged, and if clear crystals (precipitated sodium sulfite) are observed, sufficient sodium sulfite is present. If the precipitated sodium sulfite disappears, add more crystalline sodium sulfite in approximately 100-mg portions until a solid residue remains after repeated shaking.

7.3.4 Add 5 mL distilled water and shake for at least 1 min. Allow the sample to stand for 5-10 min. Transfer the hexane layer (top) to a concentrator tube and use the K-D technique to concentrate the extract to 1.0 mL.

7.4 Analyze the cleaned up extracts by gas chromatography (see the determinative methods, Section 4.3 of this chapter).

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 3600 for cleanup procedures.

8.2 All reagents should be checked prior to use to verify that interferences do not exist.

9.0 METHOD PERFORMANCE

9.1 Table 1 indicates the effect of using copper and mercury to remove sulfur on the recovery of certain pesticides.

10.0 REFERENCES

1. Loy, E.W., private communication.

2. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9 (1971).

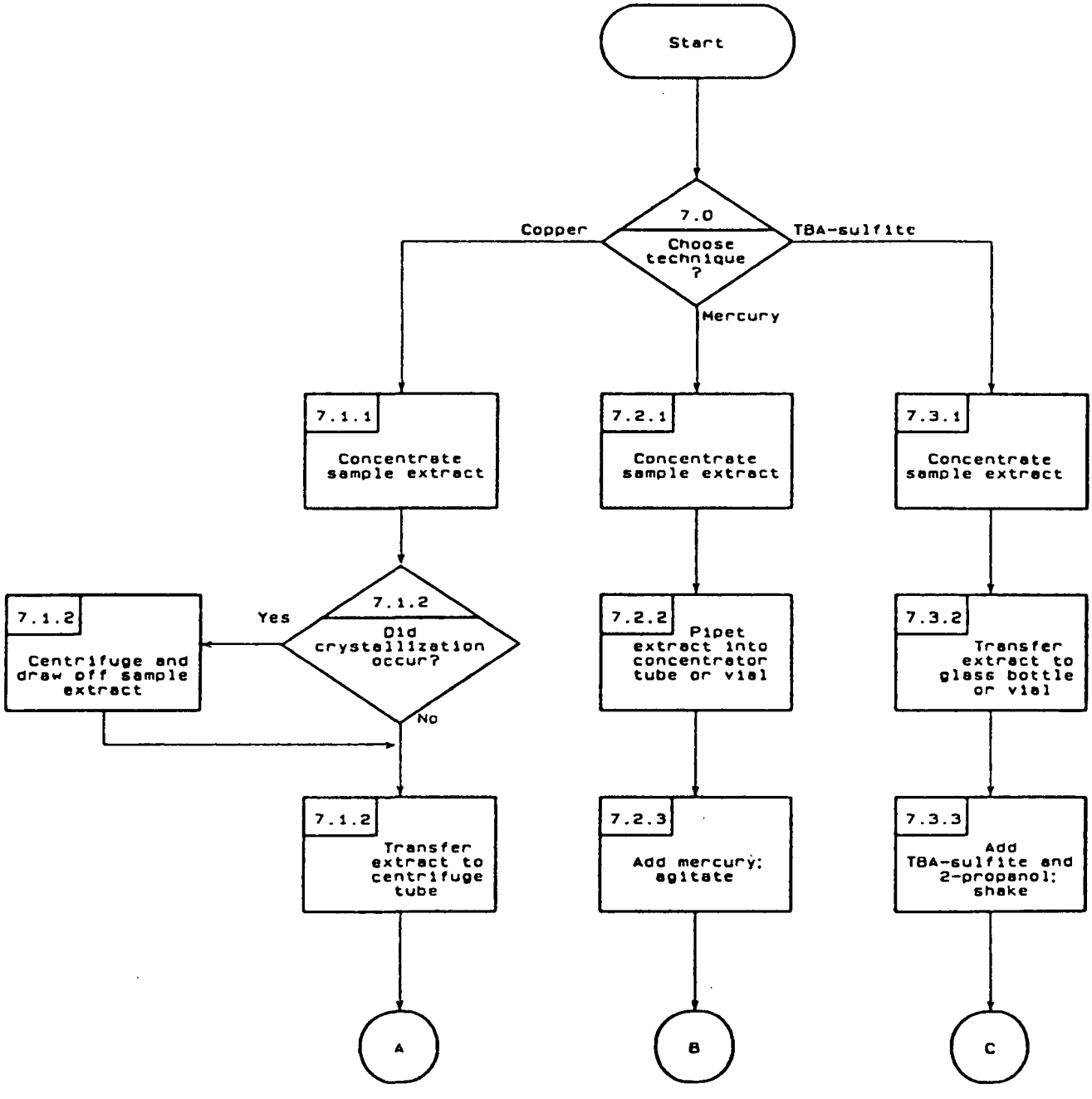
3. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, Revision, July 1985.

Table 1. EFFECT OF MERCURY AND COPPER ON PESTICIDES

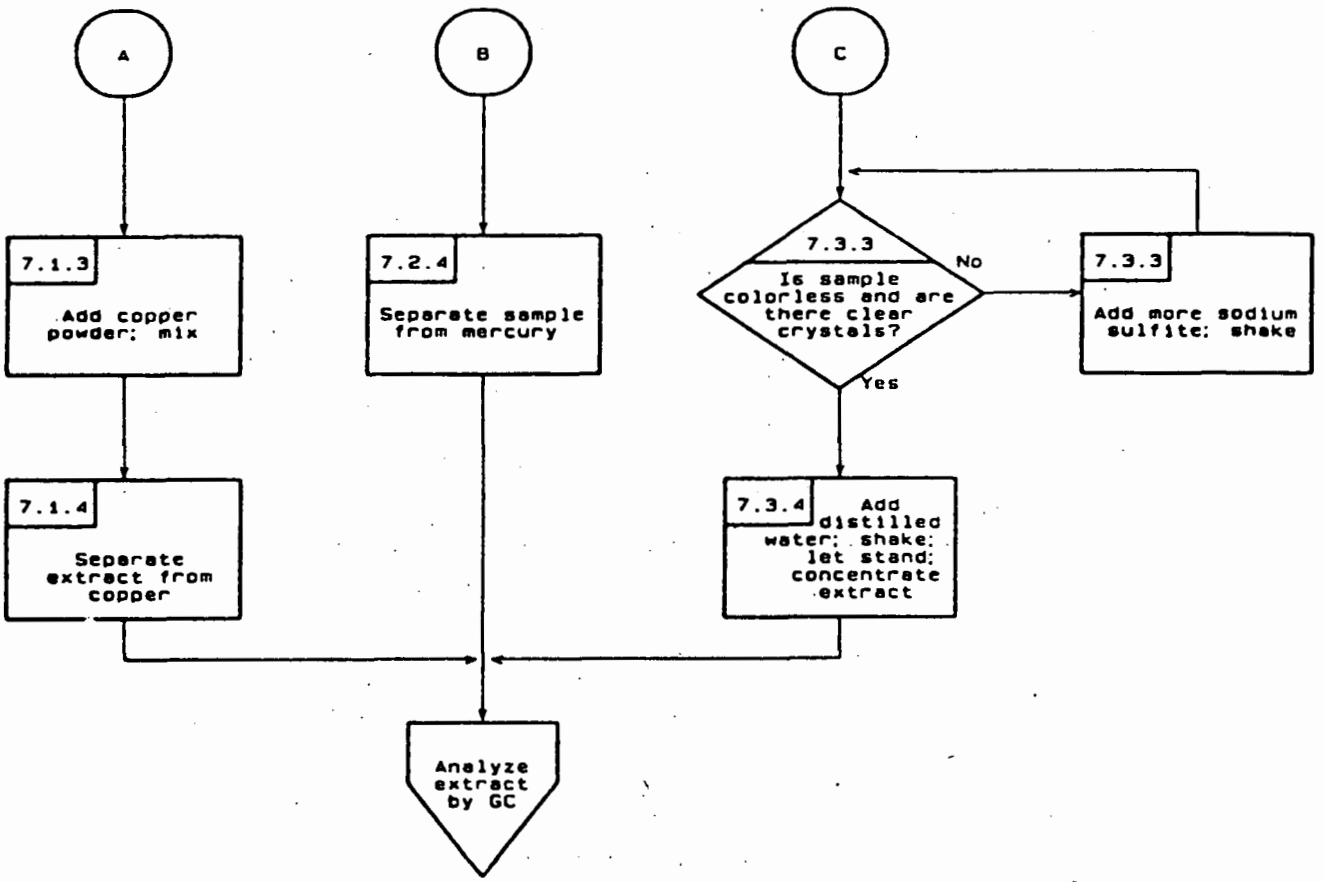
Pesticide	Percent Recovery[a] using: Mercury	Copper
Aroclor 1254	97.10	104.26
Lindane	75.73	94.83
Heptachlor	39.84	5.39
Aldrin	95.52	93.29
Heptachlor epoxide	69.13	96.55
DDE	92.07	102.91
DDT	78.78	85.10
BHC	81.22	98.08
Dieldrin	79.11	94.90
Endrin	70.83	89.26
Chlorobenzilate	7.14	0.00
Malathion	0.00	0.00
Diazinon	0.00	0.00
Parathion	0.00	0.00
Ethion	0.00	0.00
Trithion	0.00	0.00

[a] Percent recoveries cited are averages based on duplicate analyses for all compounds other than for Aldrin and BHC. For Aldrin, four and three determinations were averaged to obtain the result for mercury and copper, respectively. Recovery of BHC using copper is based on one analysis.

METHOD 3660
SULFUR CLEANUP



Revision 0
Date September 1986


A
B
C
7.1.3
Add copper powder; mix
7.2.4
Separate sample from mercury
7.3.3
Is sample colorless and are there clear crystals?
No
7.3.3
Add more sodium sulfite; shake
Yes
7.1.4
Separate extract from copper
7.3.4
Add distilled water; shake; let stand; concentrate extract
Analyze extract by GC

4.3 DETERMINATION OF ORGANIC ANALYTES

4.3.1 GAS CHROMATOGRAPHIC METHODS

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 reagent water or solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a solvent blank or of reagent 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 Section 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, Section 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 (Section 7.4.2) or the internal standard technique (Section 7.4.3).

7.4.2 **External standard calibration procedure:**

7.4.2.1 For each 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- to 5-uL 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 ±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-hr period. Serial injections over less than a 72-hr 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 Paragraph 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 Section 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 Section 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 Section 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 (Paragraph 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 Section 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 Section 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 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 Paragraph 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 Paragraph 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 water 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 matrix spike duplicate/duplicate 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 Section 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 Section 7.4 sets a limit of ±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 Section 7.5 requires the establishment of retention time windows.

8.5.4 Paragraph 7.6.8 sets a limit of ±15% difference when comparing the initial response of a given analyte versus any succeeding standards analyzed during an analysis sequence.

8.5.5 Paragraph 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 uL of the QC check sample concentrate (Section 8.6.1) to 100 mL of reagent 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 (8.6.1) to each of four 1-L aliquots of reagent 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 ug/L, and the standard deviation of the recovery (s) in ug/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 Section 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 Section 8.6.2.

8.6.6.2 Beginning with Section 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 Section 8.6.2.

8.7 The laboratory must, on an ongoing basis, spike at least one sample per analytical batch (maximum of 20 samples per batch) to assess accuracy. 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 Section 8.7.2, whichever concentration would be larger.

8.7.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at the same concentration as the QC check sample (8.6.2) or 1 to 5 times higher than the background concentration determined in Section 8.7.2, whichever concentration would be larger.

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 check sample concentration (Section 8.6.2).

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 check sample concentrate (Section 8.6.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check 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 Semivolatile 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 check sample concentrate (Section 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 check 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 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 check sample concentration (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 $\bar{X}$; (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 Section 8.8.

8.8 If any analyte fails the acceptance criteria for recovery in Section 8.7, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of 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 Section 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 standard:** For volatile organics, add 10 uL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 5 mL of reagent water. For semivolatile organics, add 1.0 mL of the QC check sample concentrate (Section 8.6.1 or 8.7.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.7. Prepare the QC check standard for analysis following the guidelines given in Method 3500 (e.g., purge-and-trap, extraction, etc.).

8.8.2 Analyzed the QC check standard 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 Section 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 Section 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 (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:

Upper Control Limit (UCL) = p + 3s
Lower Control Limit (LCL) = p - 3s

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 Paragraph 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 reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

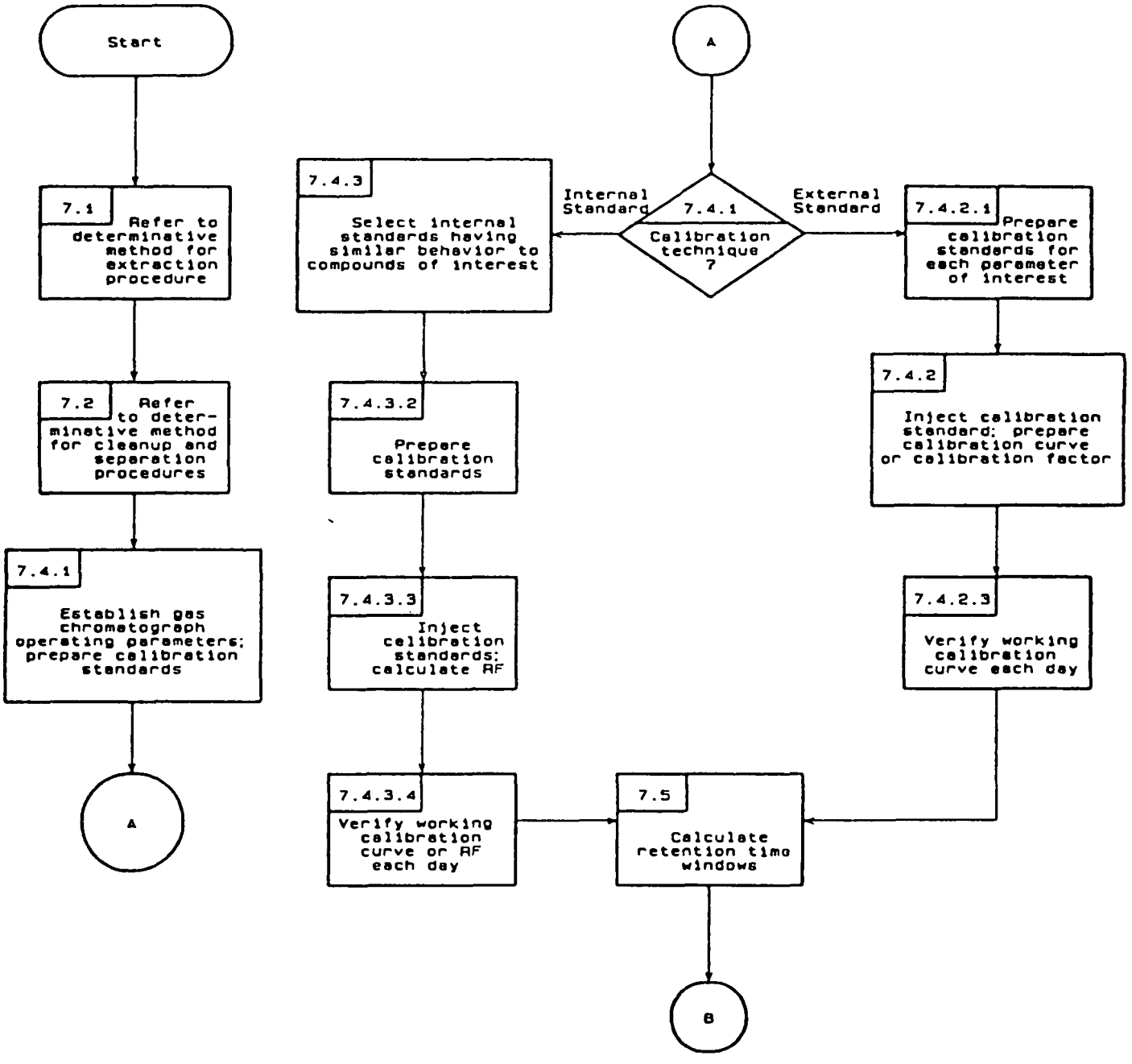
9.2 Refer to the determinative method for specific method performance information.

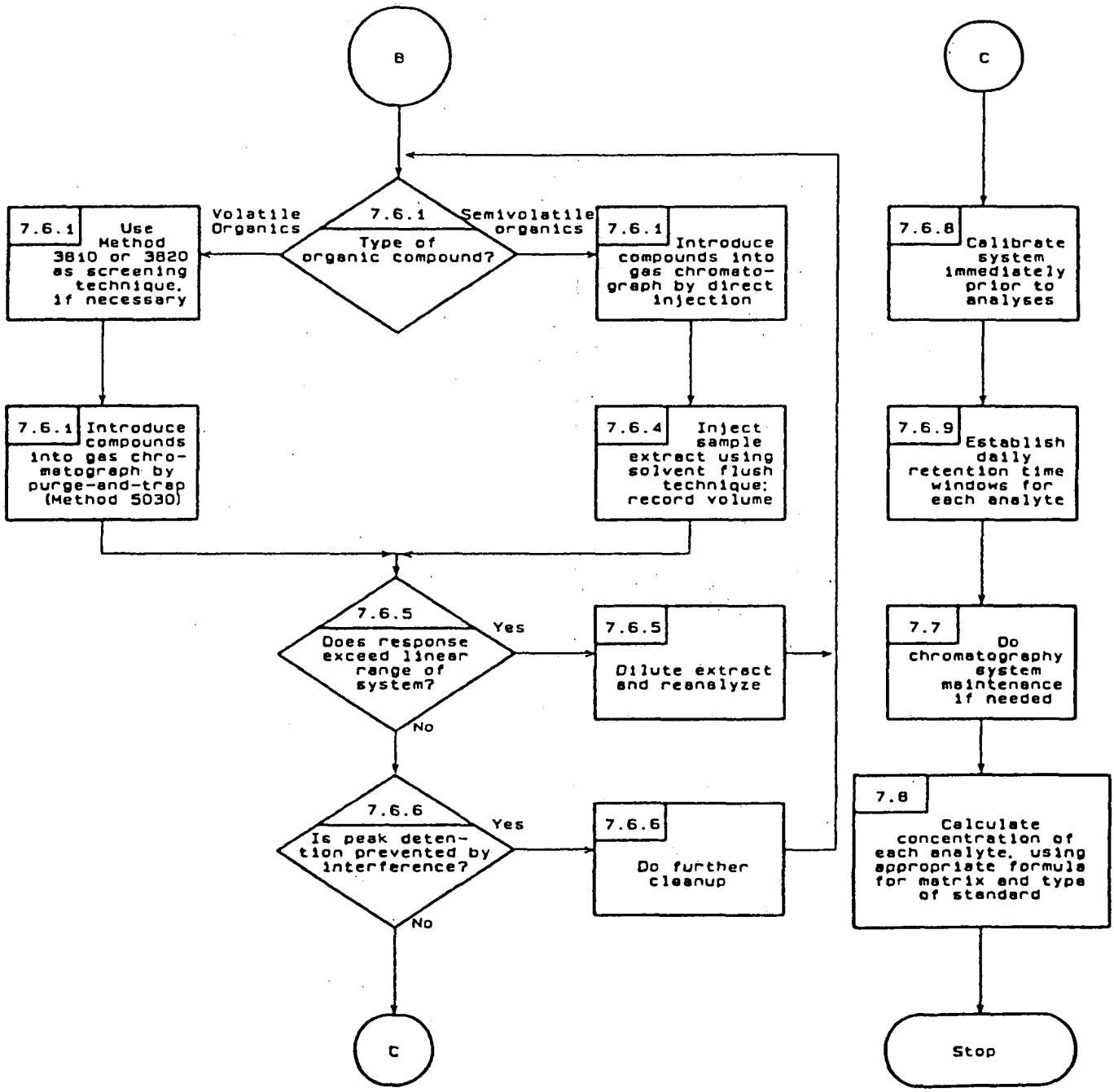
10.0 REFERENCES

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.


Start
7.1
Refer to determinative method for extraction procedure
7.2
Refer to determinative method for cleanup and separation procedures
7.4.1
Establish gas chromatograph operating parameters; prepare calibration standards
A
A
7.4.1
Calibration technique ?
Internal Standard
External Standard
7.4.3
Select internal standards having similar behavior to compounds of interest
7.4.3.2
Prepare calibration standards
7.4.3.3
Inject calibration standards; calculate RF
7.4.3.4
Verify working calibration curve or RF each day
7.4.2.1
Prepare calibration standards for each parameter of interest
7.4.2
Inject calibration standard; prepare calibration curve or calibration factor
7.4.2.3
Verify working calibration curve each day
7.5
Calculate retention time windows
B


B
C
7.6.1
Type of organic compound?
Volatile Organics
Semivolatile organics
7.6.1 Use Method 3810 or 3820 as screening technique, if necessary
7.6.1 Introduce compounds into gas chromatograph by direct injection
7.6.8 Calibrate system immediately prior to analyses
7.6.1 Introduce compounds into gas chromatograph by purge-and-trap (Method 5030)
7.6.4 Inject sample extract using solvent flush technique; record volume
7.6.9 Establish daily retention time windows for each analyte
7.6.5
Does response exceed linear range of system?
Yes
No
7.6.5 Dilute extract and reanalyze
7.7 Do chromatography system maintenance if needed
7.6.6
Is peak detention prevented by interference?
Yes
No
7.6.6 Do further cleanup
7.8 Calculate concentration of each analyte, using appropriate formula for matrix and type of standard
C
Stop

METHOD 8010

HALOGENATED VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8010 is used to determine the concentration of various volatile halogenated organic compounds. Table 1 indicates compounds that may be analyzed by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical 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 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 halogen-specific detector (HSD).

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 detector, analytical columns, recorder, gases, and syringes. A data system for measuring peak heights and/or peak areas is recommended.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR HALOGENATED VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Benzyl chloride			
Bis(2-chloroethoxy)methane			
Bis(2-chloroisopropyl)ether			
Bromobenzene			
Bromodichloromethane	13.7	14.6	0.10
Bromoform	19.2	19.2	0.20
Bromomethane			
Carbon tetrachloride	13.0	14.4	0.12
Chloroacetaldehyde			
Chlorobenzene	24.2	18.8	0.25
Chloroethane	3.33	8.68	0.52
Chloroform	10.7	12.1	0.05
1-Chlorohexane			
2-Chloroethyl vinyl ether	18.0		0.13
Chloromethane	1.50	5.28	0.08
Chloromethylmethyl ether			
Chlorotoluene			
Dibromochloromethane	16.5	16.6	0.09
Dibromomethane			
1,2-Dichlorobenzene	34.9	23.5	0.15
1,3-Dichlorobenzene	34.0	22.4	0.32
1,4-Dichlorobenzene	35.4	22.3	0.24
Dichlorodifluoromethane			
1,1-Dichloroethane	9.30	12.6	0.07
1,2-Dichloroethane	11.4	15.4	0.03
1,1-Dichloroethylene	8.0	7.72	0.13
trans-1,2-Dichloroethylene	10.1	9.38	0.10
Dichloromethane			
1,2-Dichloropropane	14.9	16.6	0.04
trans-1,3-Dichloropropylene	15.2	16.6	0.34
1,1,2,2-Tetrachloroethane	21.6		0.03
1,1,1,2-Tetrachloroethane			
Tetrachloroethylene	21.7	15.0	0.03
1,1,1-Trichloroethane	12.6	13.1	0.03
1,1,2-Trichloroethane	16.5	18.1	0.02
Trichloroethylene	15.8	13.1	0.12
Trichlorofluoromethane	7.18		
Trichloropropane			
Vinyl chloride	2.67	5.28	0.18

[a] Using purge-and-trap method (Method 5030).

2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

trix	Factor[b]
water	10
vel soil	10
miscible liquid waste	500
evel soil and sludge	1250
ter miscible waste	1250

Sample PQLs are highly matrix-dependent. The PQLs listed herein are rovided for guidance and may not always be achievable.

PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-queous samples, the factor is on a wet-weight basis.

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 chemically bonded n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

4.1.3 **Detector:** Electrolytic conductivity (HSD).

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: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10-, 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 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 of the toxicity of these materials should be prepared in a hood.

5.2.1 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 0.1 mg.

5.2.2 Add the assayed reference material, as described below.

5.2.2.1 **Liquids:** Using a 100-uL 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.

5.2.2.2 **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.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

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

5.2.5 Prepare fresh standards every 2 months for gases or for reactive compounds such as 2-chloroethylvinyl ether. All other standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 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.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in 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 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.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 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).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 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).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 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.

5.5 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 (Paragraph 5.6) have been used successfully as internal standards, because of their generally unique retention times.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. 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.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 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 surrogate halocarbons. A combination of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/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 (Paragraph 5.5.2).

5.7 Methanol: 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, 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-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 min; then program an 8°C/min temperature rise to 220°C and hold for 15 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 50°C for 3 min; then program a 6°C/min temperature rise to 170°C and hold for 4 min.

7.3 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 Paragraph 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 Paragraph 7.4.1.1). 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. The detection limit is very high (approximately 10,000 ug/L) therefore, it is only

permitted where 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 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-level 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 Calculation of concentration is covered in Section 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 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 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 10 ug/mL 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, Section 8.10).

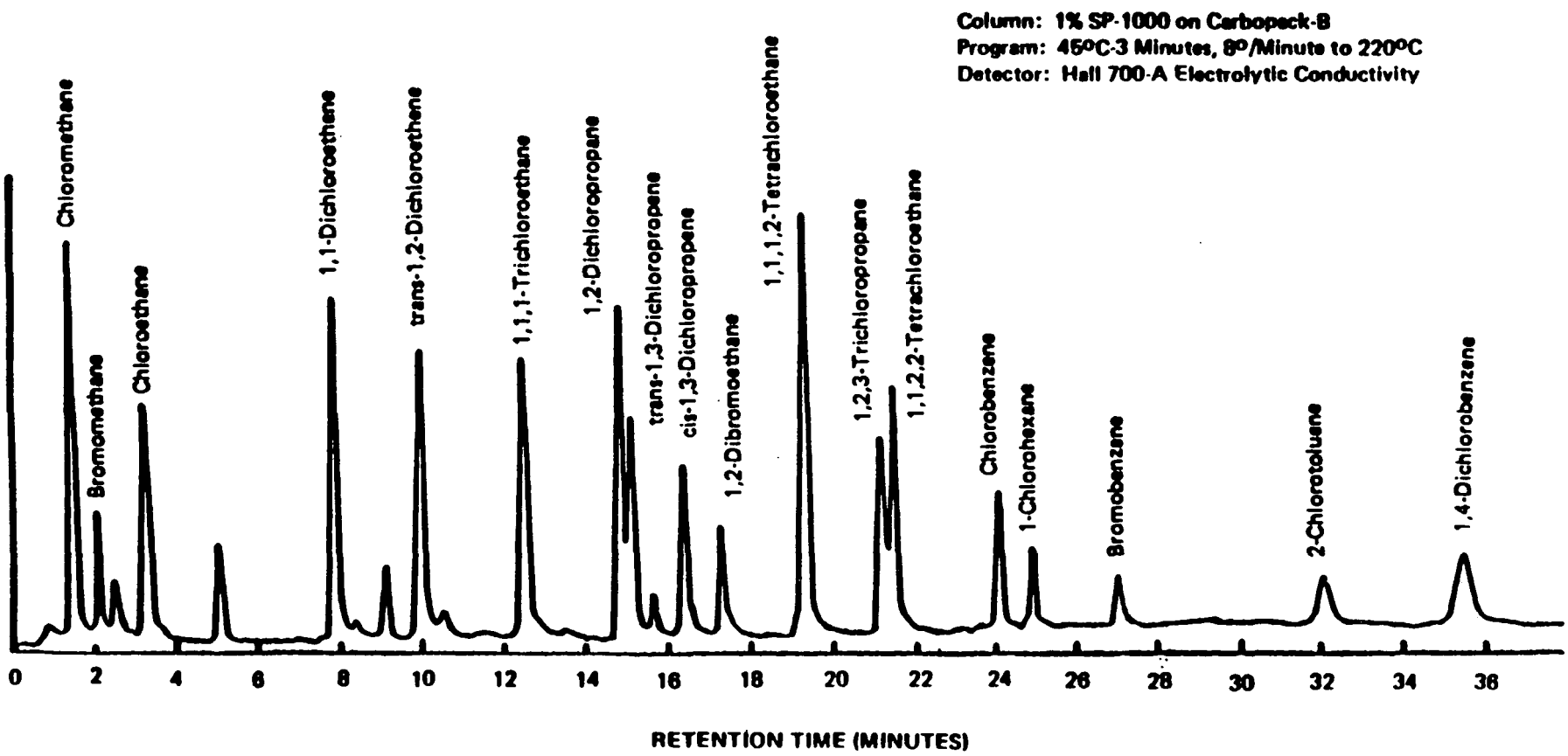


Figure 1. Gas Chromatogram of halogenated volatile organics.

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 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 8.0-500 ug/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. 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. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

6. "EPA Method Validation Study 23, Method 601 (Purgeable Halocarbons)," Report for EPA Contract 68-03-2856 (in preparation).

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 (%)
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
1,2-Dichloropropane	14.8-25.2	5.2	10.1-29.9	44-156
cis-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
trans-1,3-Dichloropropene	12.8-27.2	7.3	6.2-33.8	22-178
Methylene chloride	15.5-24.5	4.0	7.0-27.6	25-162
1,1,2,2-Tetrachloroethane	9.8-30.2	9.2	6.6-31.8	8-184
Tetrachloroethene	14.0-26.0	5.4	8.1-29.6	26-162
1,1,1-Trichloroethane	14.2-25.8	4.9	10.8-24.8	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 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.

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 ug/L.

TABLE 4. 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)
Bromodichloromethane	1.12C-1.02	0.11$\bar{X}$+0.04	0.20$\bar{X}$+1.00
Bromoform	0.96C-2.05	0.12$\bar{X}$+0.58	0.21$\bar{X}$+2.41
Bromomethane	0.76C-1.27	0.28$\bar{X}$+0.27	0.36$\bar{X}$+0.94
Carbon tetrachloride	0.98C-1.04	0.15$\bar{X}$+0.38	0.20$\bar{X}$+0.39
Chlorobenzene	1.00C-1.23	0.15$\bar{X}$-0.02	0.18$\bar{X}$+1.21
Chloroethane	0.99C-1.53	0.14$\bar{X}$-0.13	0.17$\bar{X}$+0.63
2-Chloroethyl vinyl ether[b]	1.00C	0.20$\bar{X}$	0.35$\bar{X}$
Chloroform	0.93C-0.39	0.13$\bar{X}$+0.15	0.19$\bar{X}$-0.02
Chloromethane	0.77C+0.18	0.28$\bar{X}$-0.31	0.52$\bar{X}$+1.31
Dibromochloromethane	0.94C+2.72	0.11$\bar{X}$+1.10	0.24$\bar{X}$+1.68
1,2-Dichlorobenzene	0.93C+1.70	0.20$\bar{X}$+0.97	0.13$\bar{X}$+6.13
1,3-Dichlorobenzene	0.95C+0.43	0.14$\bar{X}$+2.33	0.26$\bar{X}$+2.34
1,4-Dichlorobenzene	0.93C-0.09	0.15$\bar{X}$+0.29	0.20$\bar{X}$+0.41
1,1-Dichloroethane	0.95C-1.08	0.08$\bar{X}$+0.17	0.14$\bar{X}$+0.94
1,2-Dichloroethane	1.04C-1.06	0.11$\bar{X}$+0.70	0.15$\bar{X}$+0.94
1,1-Dichloroethene	0.98C-0.87	0.21$\bar{X}$-0.23	0.29$\bar{X}$-0.04
trans-1,2-Dichloroethene	0.97C-0.16	0.11$\bar{X}$+1.46	0.17$\bar{X}$+1.46
1,2-Dichloropropane[b]	1.00C	0.13$\bar{X}$	0.23$\bar{X}$
cis-1,3-Dichloropropene[b]	1.00C	0.18$\bar{X}$	0.32$\bar{X}$
trans-1,3-Dichloropropene[b]	1.00C	0.18$\bar{X}$	0.32$\bar{X}$
Methylene chloride	0.91C-0.93	0.11$\bar{X}$+0.33	0.21$\bar{X}$+1.43
1,1,2,2-Tetrachloroethene	0.95C+0.19	0.14$\bar{X}$+2.41	0.23$\bar{X}$+2.79
Tetrachloroethene	0.94C+0.06	0.14$\bar{X}$+0.38	0.18$\bar{X}$+2.21
1,1,1-Trichloroethane	0.90C-0.16	0.15$\bar{X}$+0.04	0.20$\bar{X}$+0.37
1,1,2-Trichloroethane	0.86C+0.30	0.13$\bar{X}$-0.14	0.19$\bar{X}$+0.67
Trichloroethene	0.87C+0.48	0.13$\bar{X}$-0.03	0.23$\bar{X}$+0.30
Trichlorofluoromethane	0.89C-0.07	0.15$\bar{X}$+0.67	0.26$\bar{X}$+0.91
Vinyl chloride	0.97C-0.36	0.13$\bar{X}$+0.65	0.27$\bar{X}$+0.40

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.

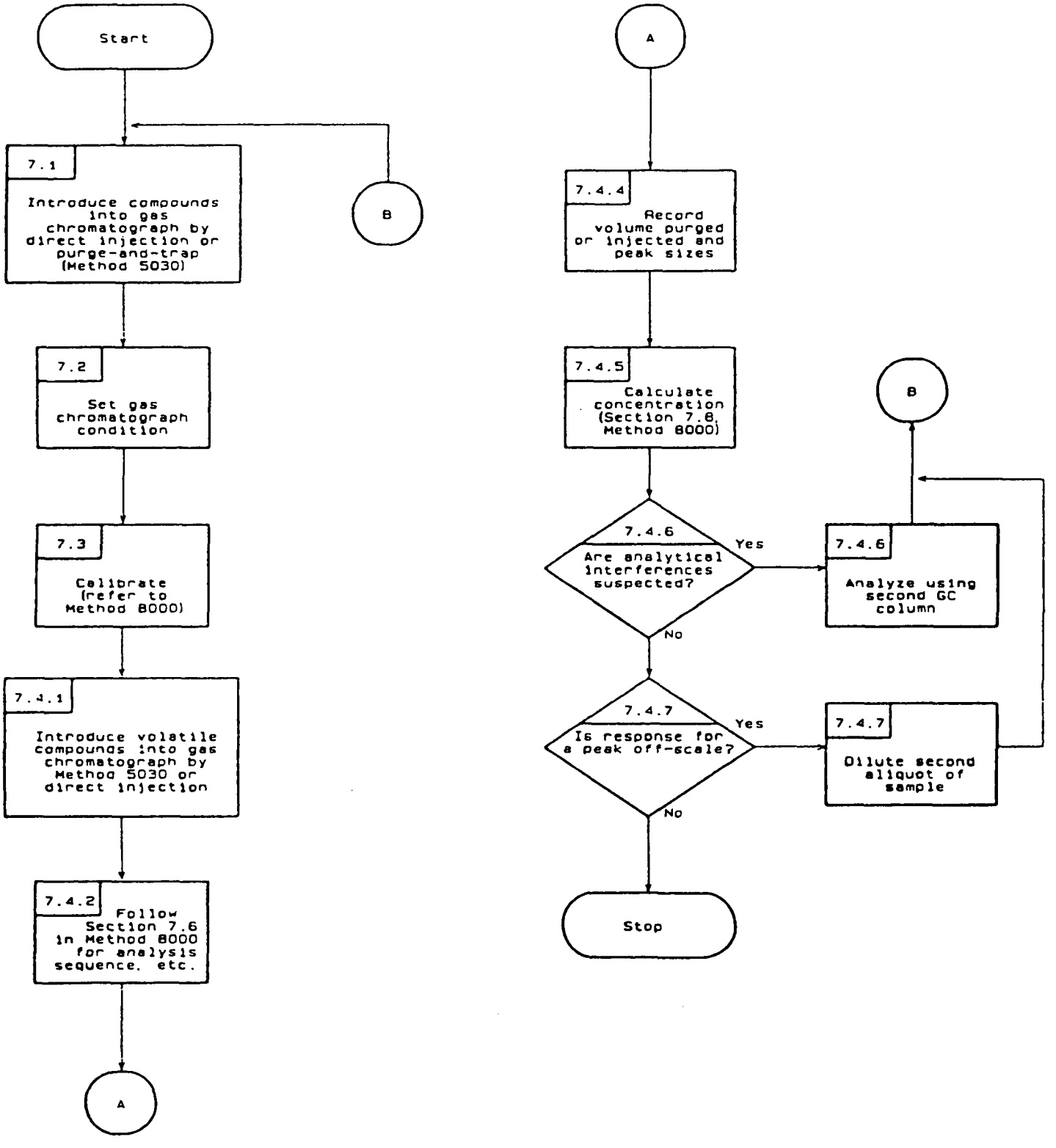
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

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.

[a]From 40 CFR Part 136 for Method 601.

[b]Estimates based upon the performance in a single laboratory.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
B
7.4.6
Are analytical interferences suspected?
Yes
7.4.6
Analyze using second GC column
No
7.4.7
Is response for a peak off-scale?
Yes
7.4.7
Dilute second aliquot of sample
No
Stop

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.

TABLE 1. NONHALOGENATED VOLATILE ORGANICS

Acrylamide
Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)
Paraldehyde (trimer of acetaldehyde)

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 flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the analytes of interest.

5.2 Stock standards: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids.

5.2.1 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 0.1 mg.

5.2.2 Using a 100-uL 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.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

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

5.2.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 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.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in 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 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.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 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).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 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).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 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.

5.5 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more inter$l 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.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. 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.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 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 recommended to encompass the range of temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/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 (Paragraph 5.5.2).

5.7 Methanol: 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, 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-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 min; then program an 8°C/min temperature rise to 220°C and hold for 15 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 50°C for 3 min; then program a 6°C/min temperature rise to 170°C and hold for 4 min.

7.3 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 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 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 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-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 Section 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 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 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 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, Section 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.

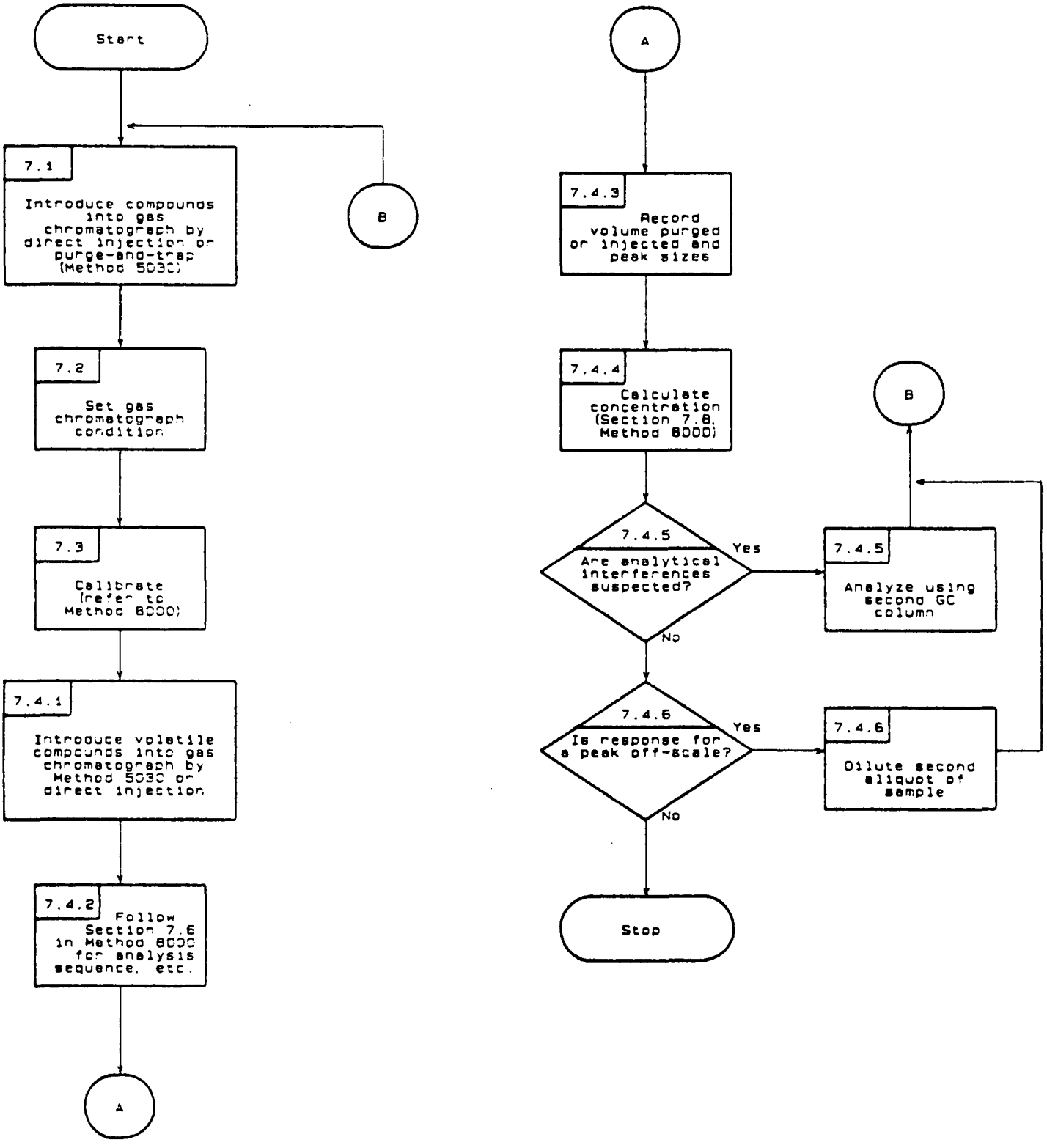
9.2 Specific method performance information will be provided as it becomes available.

10.0 REFERENCES

1. Bellar, T.A., and J.J. Lichtenberg, 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).


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.3
Record volume purged or injected and peak sizes
7.4.4
Calculate concentration (Section 7.8, Method 8000)
B
7.4.5
Are analytical interferences suspected?
Yes
7.4.5
Analyze using second GC column
No
7.4.6
Is response for a peak off-scale?
Yes
7.4.6
Dilute second aliquot of sample
No
Stop

METHOD 8020

AROMATIC VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8020 is used to determine the concentration of various aromatic volatile organic compounds. Table 1 indicates compounds which may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) 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 analyzed 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 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.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR AROMATIC VOLATILE ORGANICS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Benzene	3.33	2.75	0.2
Chlorobenzene	9.17	8.02	0.2
1,4-Dichlorobenzene	16.8	16.2	0.3
1,3-Dichlorobenzene	18.2	15.0	0.4
1,2-Dichlorobenzene	25.9	19.4	0.4
Ethyl Benzene	8.25	6.25	0.2
Toluene	5.75	4.25	0.2
Xylenes			

[a] Using purge-and-trap method (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.

4.1.2 **Columns:**

4.1.2.1 Column 1: 6-ft x 0.082-in I.D. #304 stainless steel or glass column packed with 5% SP-1200 and 1.75% Bentone-34 on 100/120 mesh Supelcort or equivalent.

4.1.2.2 Column 2: 8-ft x 0.1-in I.D. 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: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 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.

5.2.1 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 0.1 mg.

5.2.2 Using a 100-uL 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.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.2.5 All standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

5.3 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 Paragraph 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.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in 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 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.

5.4.1 Do not inject more than 20 uL of alcoholic standards into 100 mL of reagent water.

5.4.2 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).

5.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.4.4 Mix aqueous standards by inverting the flask three times only.

5.4.5 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).

5.4.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.7 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.

5.5 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 compound, alpha,alpha,alpha-trifluorotoluene recommended for use as a surrogate spiking compound (Paragraph 5.6) has been used successfully as an internal standards.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. 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.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 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 surrogate compounds (e.g, alpha,alpha,alpha-trifluorotoluene) recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/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 (Paragraph 5.5.2).

5.7 Methanol: 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, 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-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 36 mL/min flow rate. The temperature program sequences are as follows: For lower boiling compounds, operate at 50°C isothermal for 2 min; then program at 6°C/min to 90°C and hold until all compounds have eluted. For higher boiling range of compounds, operate at 50°C isothermal for 2 min; then program at 3°C/min to 110°C and hold until all compounds have eluted. Column 1 provides outstanding separations for a wide variety of aromatic hydrocarbons. Column 1 should be used as the primary analytical column because of its unique ability to resolve para-, meta-, and ortho-aromatic isomers.

7.2.2 **Column 2:** Set helium gas flow at 30 mL/min flow rate. The temperature program sequence is as follows: 40°C isothermal for 2 min; then 2°C/min to 100°C and hold until all compounds have eluted. Column 2, an extremely high-polarity column, has been used for a number of years to resolve aromatic hydrocarbons from alkanes in complex samples. However, 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 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. 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 Section 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. 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 Section 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 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 Mandatory quality control to validate the GC system operation is found in Method 8000, Section 8.6.

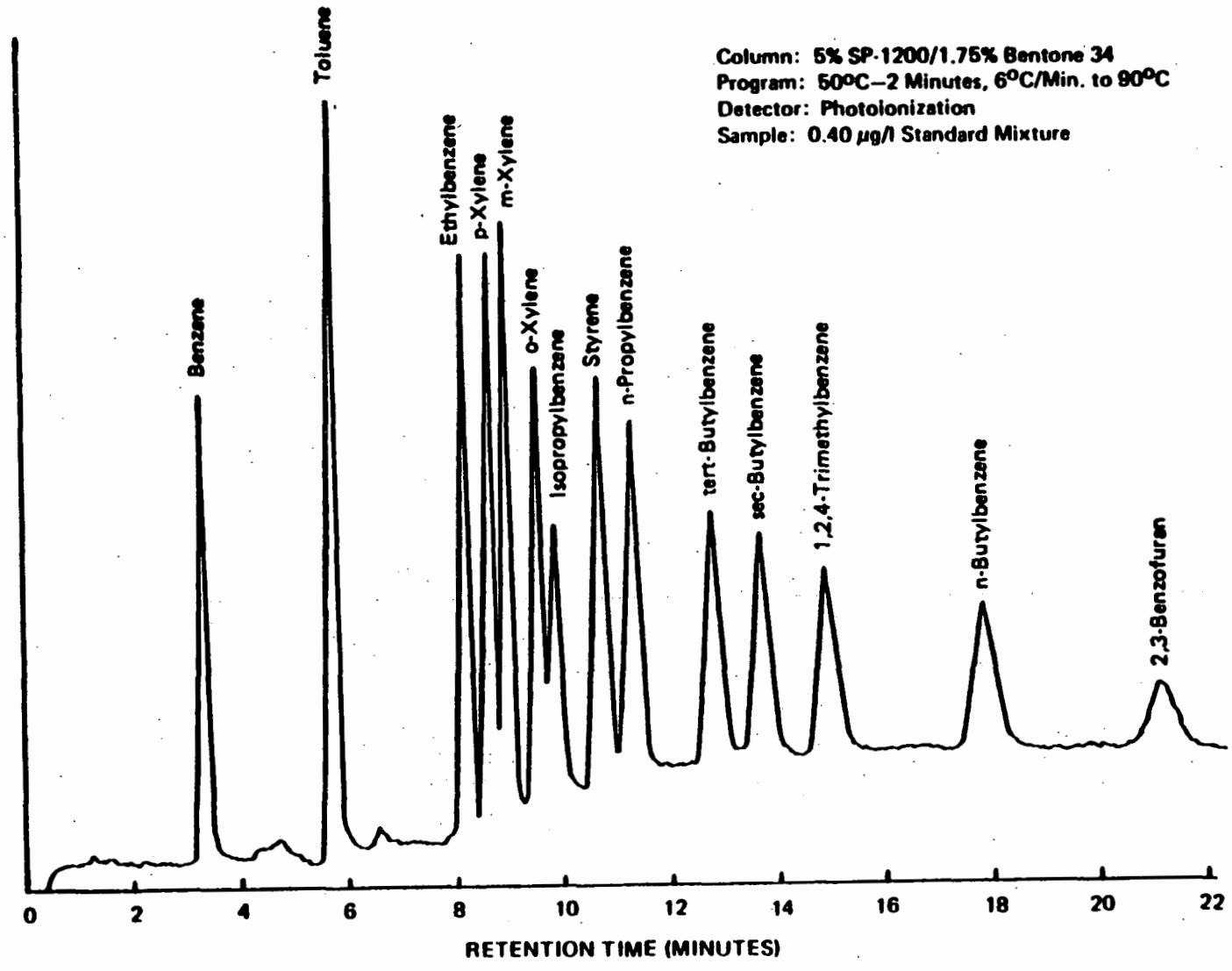


Figure 1. Chromatogram of aromatic volatile organics (column 1 conditions).

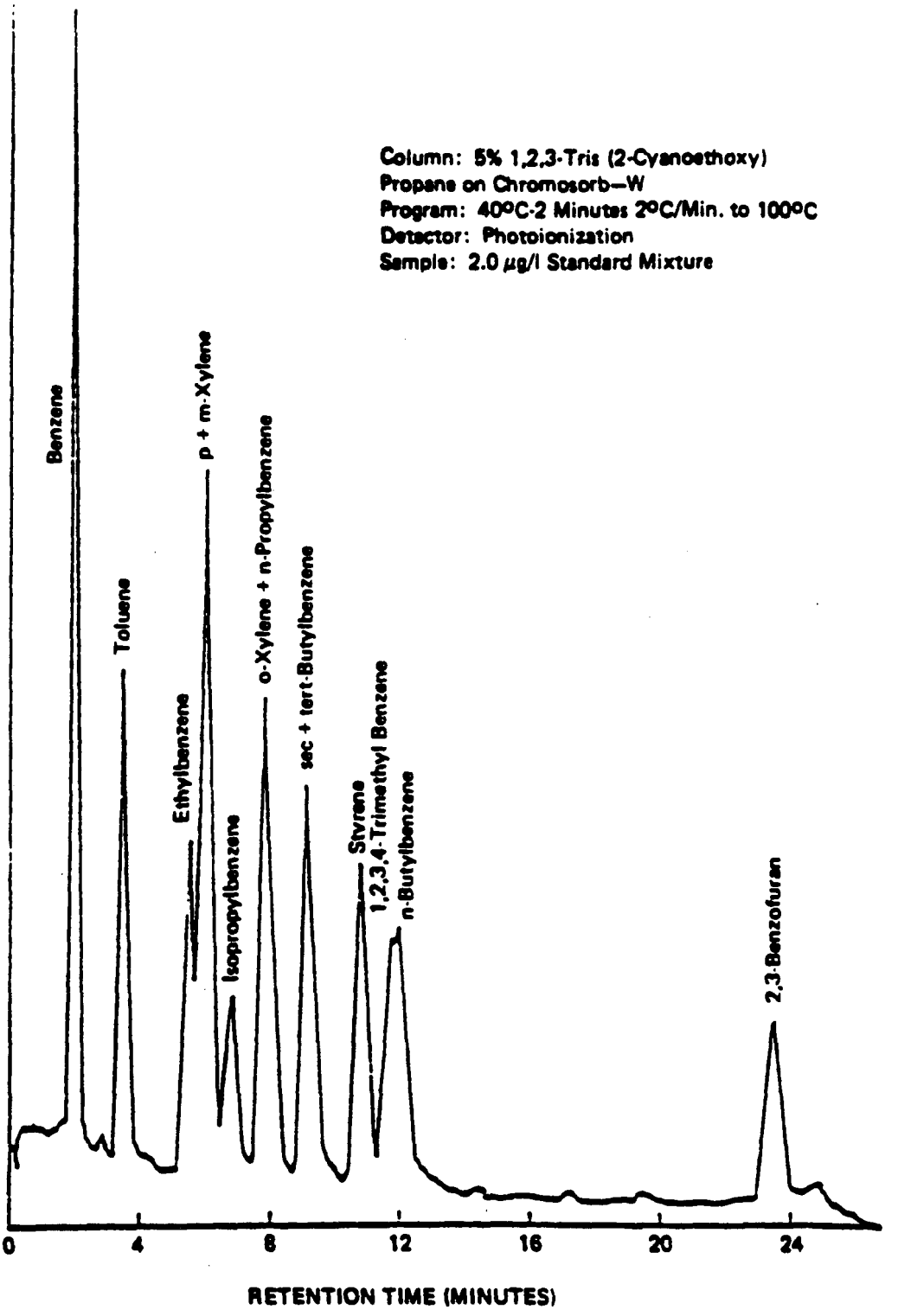


Figure 2. Chromatogram of aromatic volatile organics (column 2 conditions).

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 10 ug/mL 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, Section 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 This method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 2.1-500 ug/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.

7. Provost, L.P., and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

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 (%)
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 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 are from 40 CFR Part 136 for Method 602 and were calculated assuming a QC check sample concentration of 20 ug/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' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/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

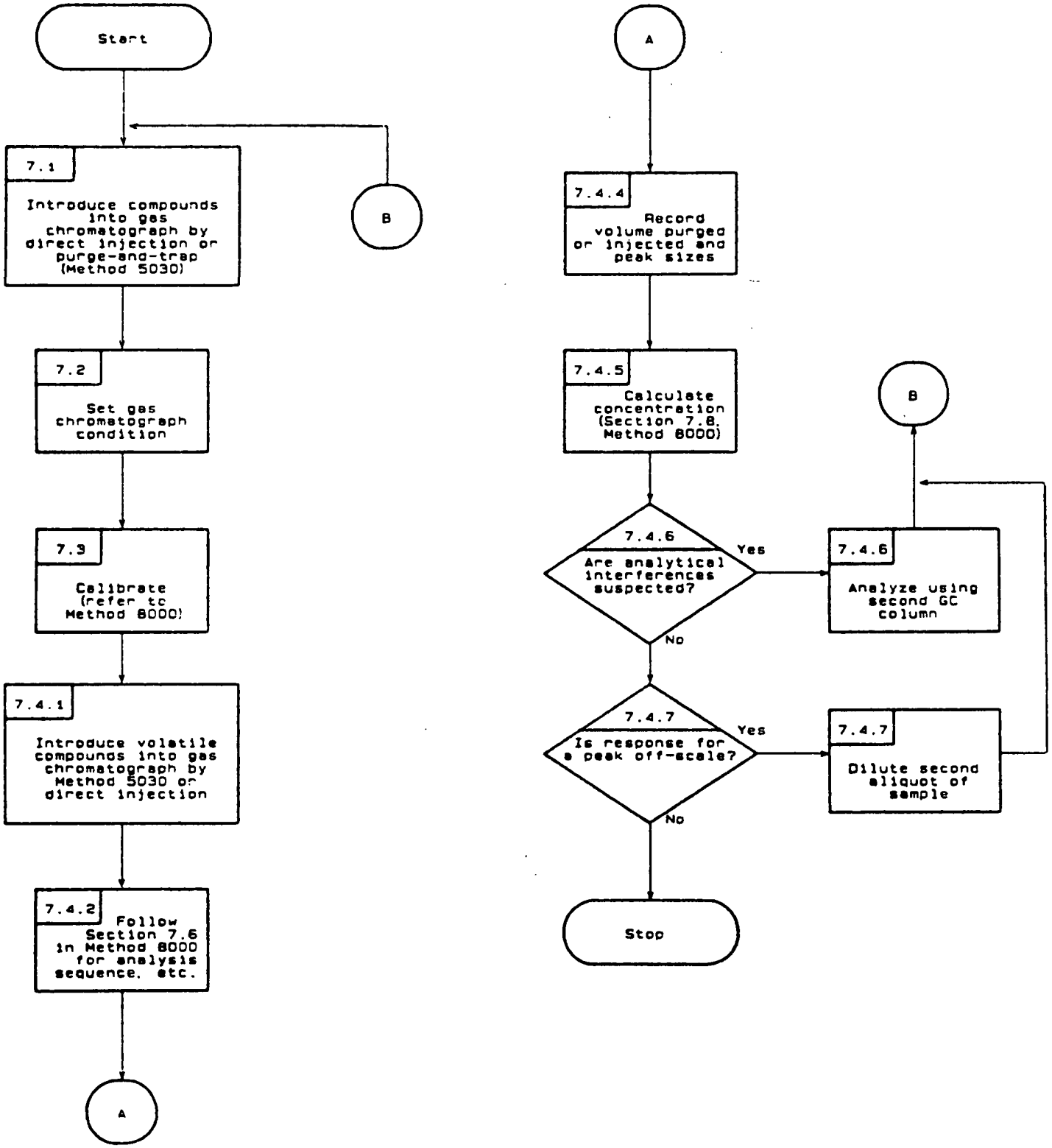
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

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.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
B
7.4.6
Are analytical interferences suspected?
Yes
7.4.6
Analyze using second GC column
No
7.4.7
Is response for a peak off-scale?
Yes
7.4.7
Dilute second aliquot of sample
No
Stop

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.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method detection limit[a] (ug/L)
Acrolein	10.6	8.2	0.7
Acrylonitrile	12.7	9.8	0.5

[a] Based 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.

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 flask: 10-, 50-, 100-, 500-, and 1,000-mL with a ground-glass stopper.

4.5 Microsyringe: 10- and 25-uL with a 0.006-in I.D. needle (Hamilton 702N or equivalent) and a 100-uL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.2 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 acrolein and acrylonitrile are lachrymators, primary dilutions of these compounds should be prepared in a hood.

5.2.1 Place about 9.8 mL of reagent water in a 10-mL tared ground-glass-stoppered volumetric flask. For acrolein standards the reagent water must be adjusted to pH 4-5 using hydrochloric acid (1:1) or sodium hydroxide (10 N), if necessary. Weigh the flask to the nearest 0.1 mg.

5.2.2 Using a 100-uL 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.

5.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

5.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap bottle. Store, with minimal headspace, at 4°C and protect from light.

5.2.5 Prepare fresh standards daily.

5.3 Secondary dilution standards: Using stock standard solutions, prepare in reagent 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 Paragraph 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.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared in 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 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.

5.4.1 Use a 25-uL Hamilton 702N microsyringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of standards into water).

5.4.2 Never use pipets to dilute or transfer samples or aqueous standards.

5.4.3 These standards must be prepared daily.

5.5 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.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Section 5.4.

5.5.2 Prepare a spiking solution containing each of the internal standards using the procedures described in Sections 5.2 and 5.3. 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.

5.5.3 Analyze each calibration standard according to Section 7.0, adding 10 uL of internal standard spiking solution directly to the syringe.

5.6 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 Section 5.2, add a volume to give 750 ug of each surrogate to 45 mL of reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/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 (Paragraph 5.5.2).

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-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 min; then heat as rapidly as possible to 150°C and hold for 20 min.

7.2.2 **Column 2:** Set helium gas flow at 40 mL/min flow rate. Set column temperature at 80°C for 4 min; then program at 50°C/min to 120°C and hold for 12 min.

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 uL 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 uL syringe may be appropriate. 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 Section 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 Section 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 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.

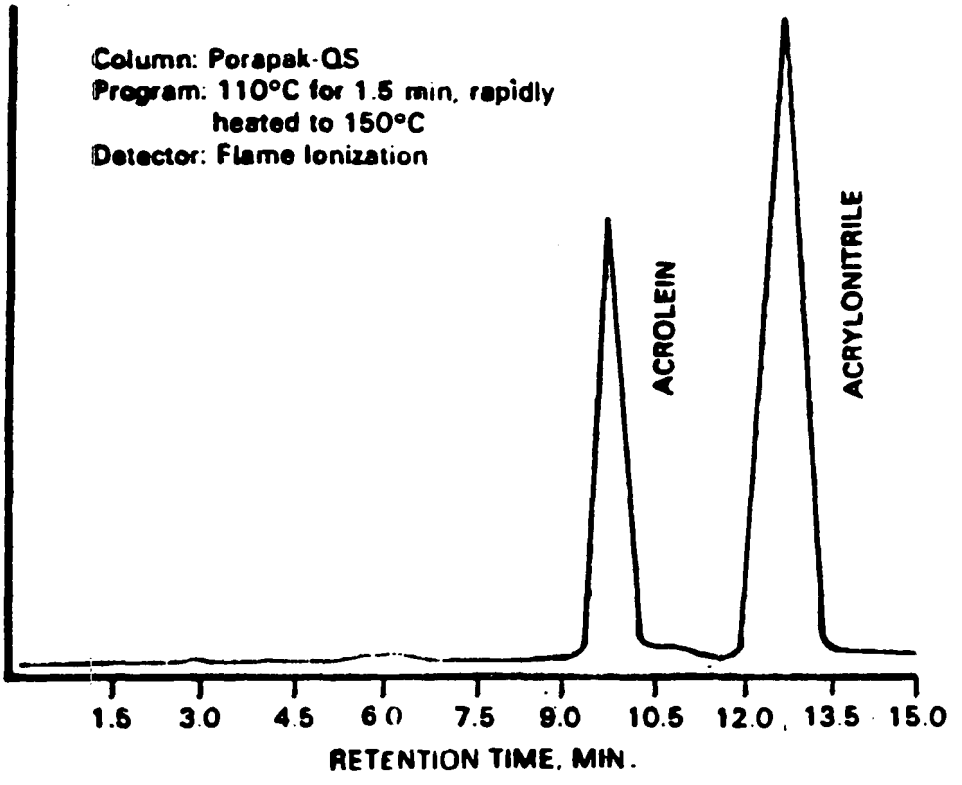


Figure 1. Gas chromatogram of acrolein and acrylonitrile.

8.2 Procedures to check the GC system operation are found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at a concentration of 25 ug/mL in reagent 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, Section 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).

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.

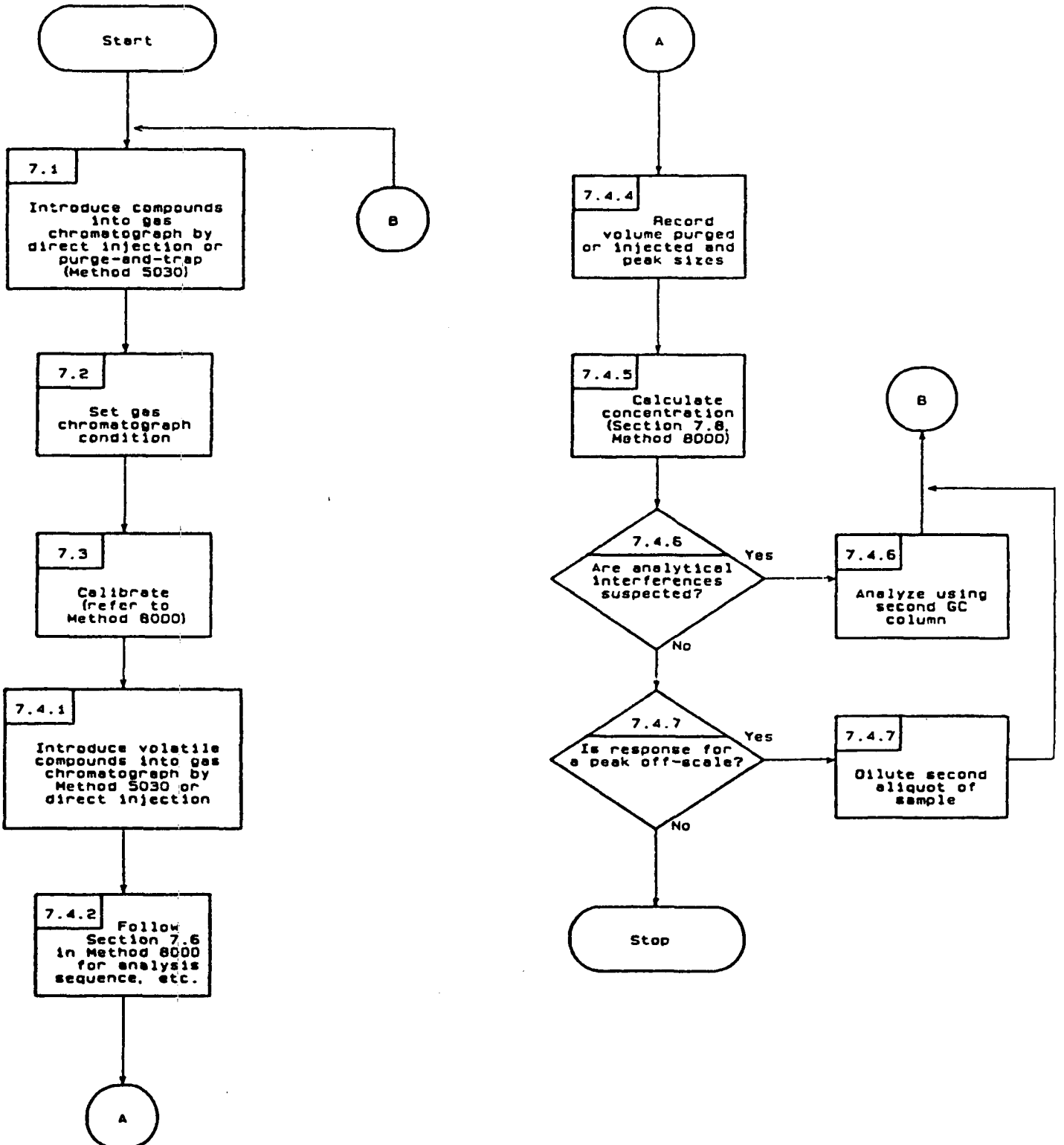
P, P_S = Percent recovery measured.

[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	RW
	50.0	51.4	0.7	103	RW
	5.0	4.0	0.2	80	POTW
	50.0	44.4	0.8	89	POTW
	5.0	0.1	0.1	2	IW
	100.0	9.3	1.1	9	IW
Acrylonitrile	5.0	4.2	0.2	84	RW
	50.0	51.4	1.5	103	RW
	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

[a]RW = Reagent water.
POTW = Prechlorination secondary effluent from a municipal sewage treatment plant.
IW = Industrial wastewater containing an unidentified acrolein reactant.


Start
7.1
Introduce compounds into gas chromatograph by direct injection or purge-and-trap (Method 5030)
B
7.2
Set gas chromatograph condition
7.3
Calibrate (refer to Method 8000)
7.4.1
Introduce volatile compounds into gas chromatograph by Method 5030 or direct injection
7.4.2
Follow Section 7.6 in Method 8000 for analysis sequence, etc.
A
A
7.4.4
Record volume purged or injected and peak sizes
7.4.5
Calculate concentration (Section 7.8, Method 8000)
7.4.6
Are analytical interferences suspected?
Yes
No
7.4.6
Analyze using second GC column
B
7.4.7
Is response for a peak off-scale?
Yes
No
7.4.7
Dilute second aliquot of sample
Stop

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 reagent water. Table 2 lists the practical quantitation limit (PQL) for other 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 running method 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

TABLE 1. FLAME IONIZATION GAS CHROMATOGRAPHY OF PHENOLS

Compound	Retention time (min)	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

[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.

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 (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

5.0 REAGENTS

5.1 Solvents: Hexane, 2-propanol, and toluene (pesticide quality or equivalent).

5.2 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.

5.2.1 **Pentafluorobenzyl bromide** (alpha-Bromopentafluorotoluene): 97% minimum purity.
NOTE: This chemical is a lachrymator.

5.2.2 **18-crown-6-ether** (1,4,7,10,13,16-Hexaoxacyclooctadecane): 98% minimum purity.
NOTE: This chemical is highly toxic.

5.3 Potassium carbonate: (ACS) Powdered.

5.4 Stock standard solutions:

5.4.1 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.

5.4.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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 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.

5.6 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 as described in Paragraph 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 2-propanol.

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 (if necessary), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent 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, Section 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, 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 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 K-D of the 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 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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 2.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min. Add an additional 2 mL of 2-propanol , 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 min.

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 Teflon-sealed screw-cap vial. 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 (Paragraph 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 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-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 Section 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 Section 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 (Paragraph 7.2.2). The derivatization and cleanup procedure is outlined in Sections 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 Paragraph 7.4.2), ng.

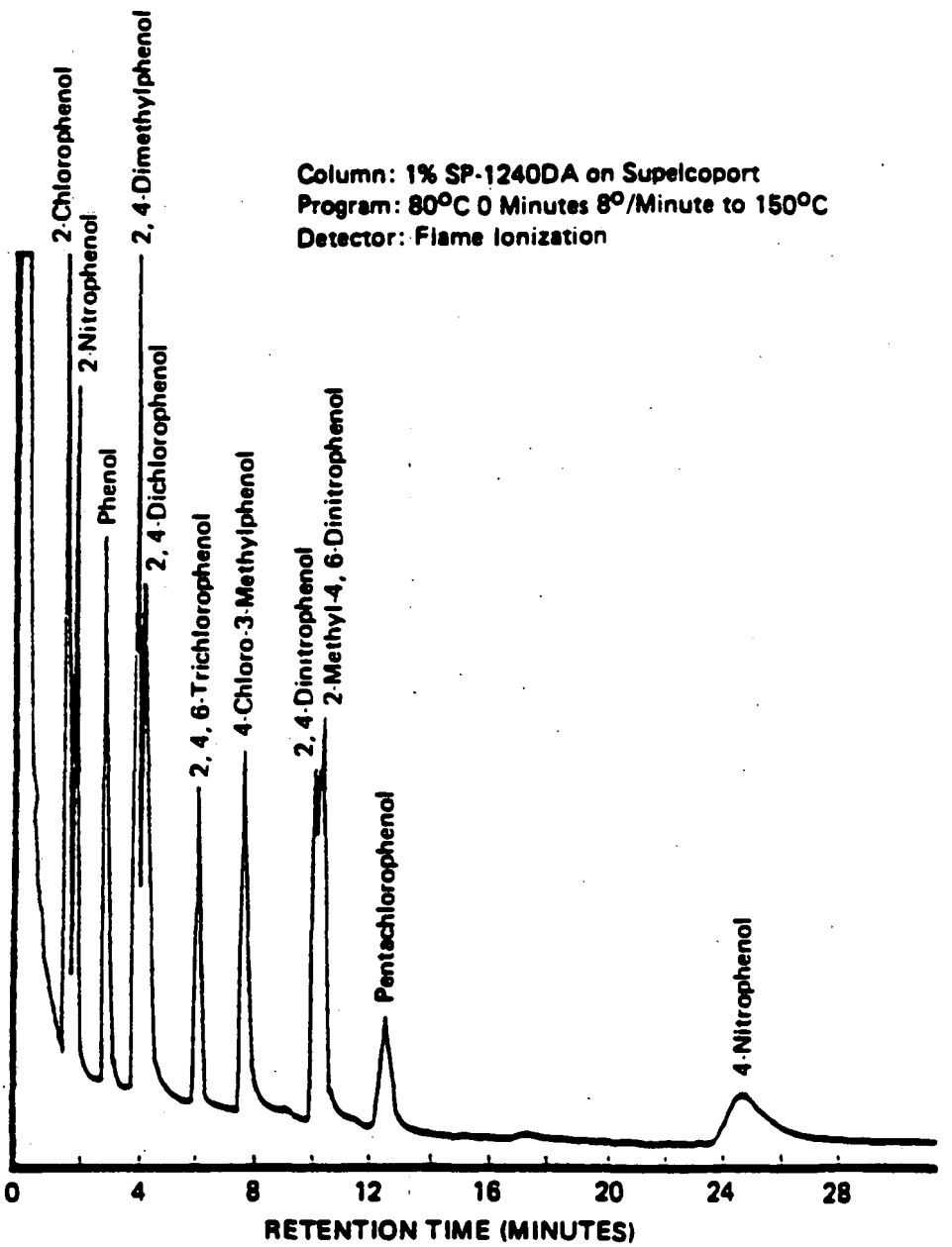


Figure 1. Gas chromatogram of phenols.

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

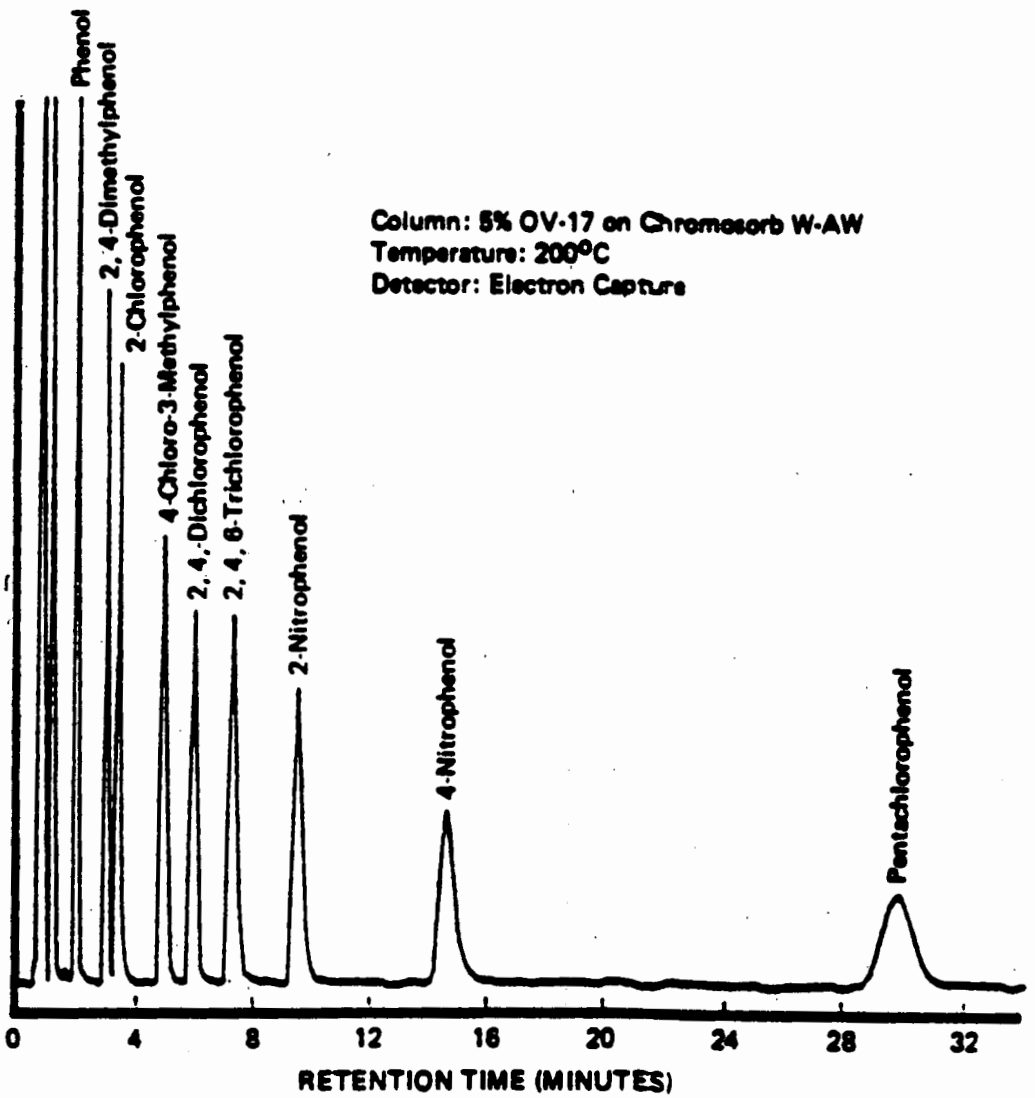


Figure 2. Gas chromatogram of PFB derivatives of phenols.

V_t = Total amount of column eluate or combined fractions from which V_i was taken, uL.

B = Total volume of hexane added in Paragraph 7.5.5, mL.

D = Total volume of 2-propanol extract prior to derivatization, mL.

V_i = Volume injected, uL.

X = Volume of water extracted, mL, or weight of nonaqueous sample extracted, g, from Section 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, Section 7.2), mL.

E = Volume of 2-propanol extract carried through derivatization in Paragraph 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 (Paragraph 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 hr 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 min. Add 3.0 mL distilled, deionized water to the reaction vial and shake for 2 min.

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 Paragraph 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, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 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, Section 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 reagent 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

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons and Category 8 - Phenols. Report for EPA Contract 68-03-2625 (in preparation).

2. 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.

3. "Determination of Phenols in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

4. "EPA Method Validation Study Test Method 604 (Phenols)," Report for EPA Contract 68-03-2625 (in preparation).

5. Kawarahara, F.K. "Microdetermination of Derivatives of Phenols and Mercaptans by Means of Electron Capture Gas Chromatography," Analytical Chemistry, 40, 1009, 1968.

6. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

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.

[a]Criteria 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.

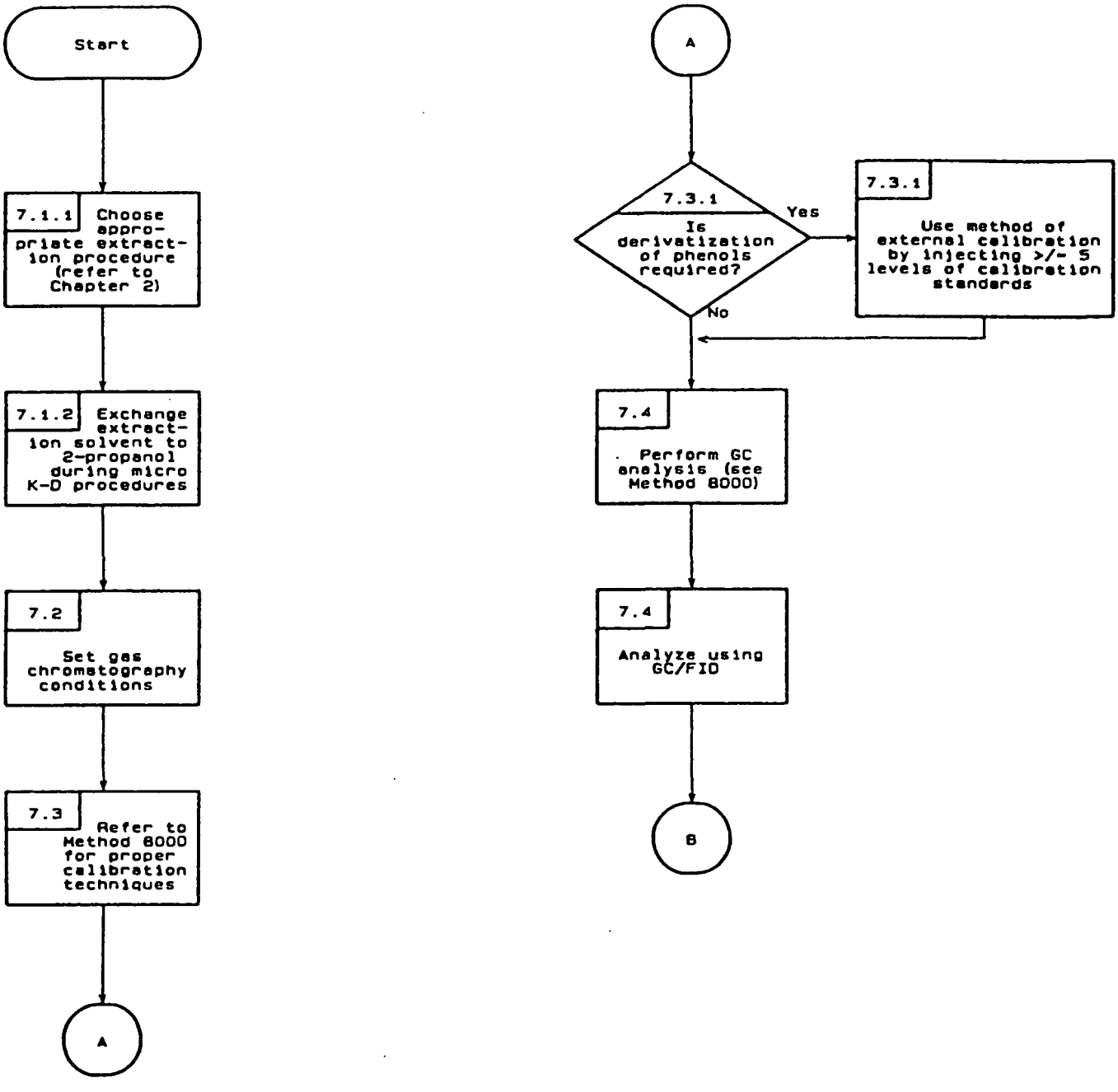
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

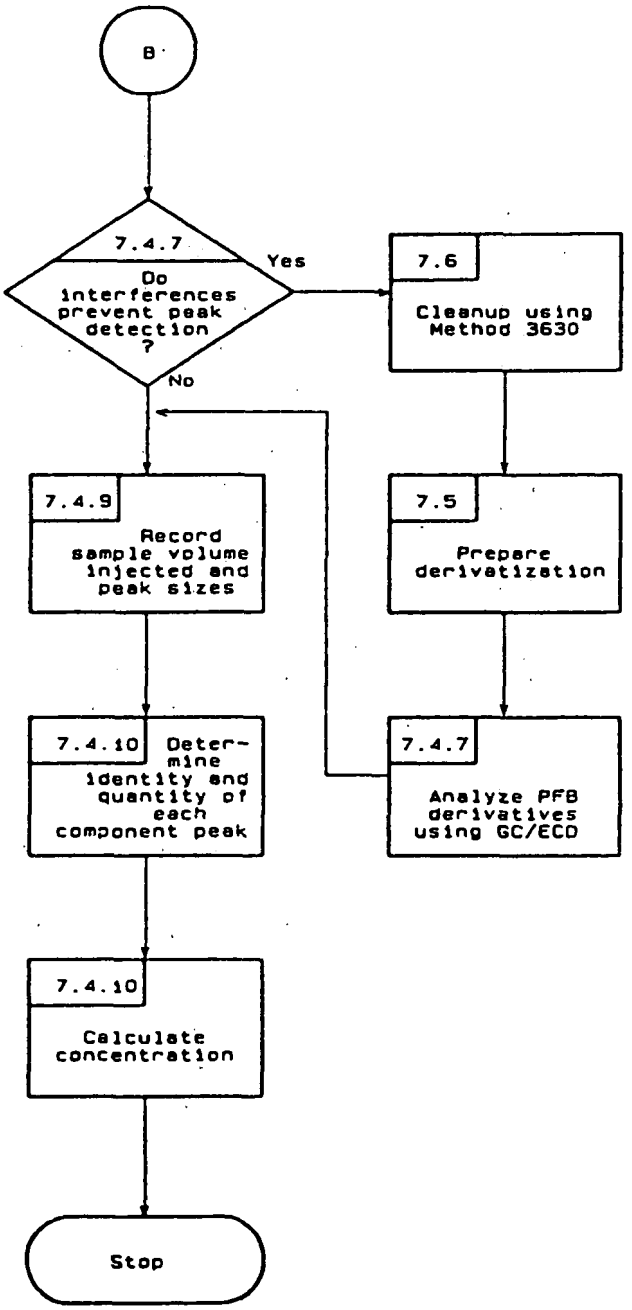
S' = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{X}$, in ug/L.

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.

[a]From 40 CFR Part 136 for Method 604.


Start
7.1.1 Choose appropriate extraction procedure (refer to Chapter 2)
7.1.2 Exchange extraction solvent to 2-propanol during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7.3.1 Is derivatization of phenols required?
Yes
No
7.3.1 Use method of external calibration by injecting >/- 5 levels of calibration standards
7.4 Perform GC analysis (see Method 8000)
7.4 Analyze using GC/FID
B


B
7.4.7
Do interferences prevent peak detection ?
Yes
No
7.6
Cleanup using Method 3630
7.4.9
Record sample volume injected and peak sizes
7.5
Prepare derivatization
7.4.10
Deter-mine identity and quantity of each component peak
7.4.7
Analyze PFB derivatives using GC/ECD
7.4.10
Calculate concentration
Stop

METHOD 8060

PHTHALATE ESTERS

1.0 SCOPE AND APPLICATION

1.1 Method 8060 is used to determine the concentration of various phthalate esters. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8060 provides gas chromatographic conditions for the detection of ppb levels of phthalate esters. Prior to use of this method, appropriate sample extraction techniques must be used. 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 an electron capture detector (ECD) or a flame ionization detector (FID). Ground water samples should be determined by ECD.

2.2 The method provides a second 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 3500, 3600, and 8000.

3.2 Phthalate esters contaminate many types of products commonly found in the laboratory. The analyst must demonstrate that no phthalate residues contaminate the sample or solvent extract under the conditions of analysis. Plastics, in particular, must be avoided because phthalates are commonly used as plasticizers and are easily extracted from plastic materials. Serious phthalate contamination may result at any time if consistent quality control is not practiced.

3.3 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 method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

3.4 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.

TABLE 1. RETENTION TIME AND DETECTION LIMIT INFORMATION FOR PHTHALATE ESTERS

Compound	Retention time (min) Col. 1[a]	Retention time (min) Col. 2[b]	Method detection limit (ug/L) ECD	Method detection limit (ug/L) FID
Benzyl butyl phthalate	*6.94	**5.11	0.34	15
Bis(2-ethylhexyl)phthalate	*8.92	**10.5	2.0	20
Di-n-butyl phthalate	8.65	3.50	0.36	14
Diethyl phthalate	2.82	1.27	0.49	31
Dimethyl phthalate	2.03	0.95	0.29	19
Di-n-octyl phthalate	*16.2	**8.0	3.0	31

[a]Column 1: Supelcoport 100/120 mesh coated with 1.5% SP-2250/1.95% SP-2401 packed in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 180°C, except where * indicates 220°C. Under these conditions the retention time of Aldrin is 5.49 min at 180°C and 1.84 min at 220°C.

[b]Column 2: Supelcoport 100/120 mesh with 3% OV-1 in a 180-cm x 4-mm I.D. glass column with carrier gas at 60 mL/min flow rate. Column temperature is 200°C, except where ** indicates 220°C. Under these conditions the retention time of Aldrin is 3.18 min at 200°C and 1.46 min at 220°C.

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

[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.

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 1: 1.8-m x 4-mm I.D. glass column packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport 100/120 mesh or equivalent.

4.1.2.2 Column 2: 1.8-m x 4-mm I.D. glass column packed with 3% OV-1 on Supelcoport 100/120 mesh or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

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 (±5°C). The bath should be used in a hood.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2- and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane 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.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration 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.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 water blank with one or two surrogates (e.g., phthalates that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 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, 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 either Method 3540 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 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. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 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 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 Teflon-sealed screw-cap vial. 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 hexane. 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 hexane 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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

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 hexane. Adjust the extract volume to 2.0 mL and proceed with either Method 3610 or 3620.

7.2 Gas chromatography conditions (Recommended): The analysis for phthalate esters may be conducted using either a flame ionization or an electron capture detector. The ECD may, however, provide substantially better sensitivity.

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Set column temperature at 180°C isothermal.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 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. Refer to Method 8000 for a description of each of these procedures.

7.3.2 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.

7.4 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 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-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for phthalate esters are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using either Method 3610 or 3620.

7.5 Cleanup:

7.5.1 Proceed with either Method 3610 or 3620, using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

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, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte of interest at the following concentrations in acetone: butyl benzyl phthalate, 10 ug/mL; bis(2-ethylhexyl) phthalate, 50 ug/mL; di-n-octyl phthalate, 50 ug/mL; and any other phthalate, 25 ug/mL.

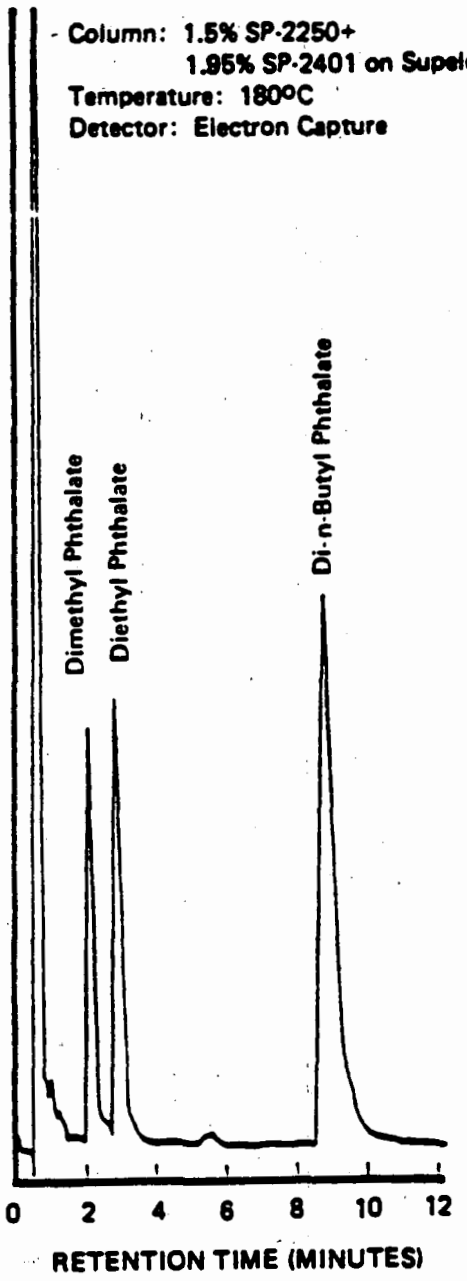


Figure 1. Gas chromatogram of phthalates (example 1).

Column: 1.5% SP-2250+
1.95% SP-2401 on Supelcoport
Temperature: 180°C
Detector: Electron Capture

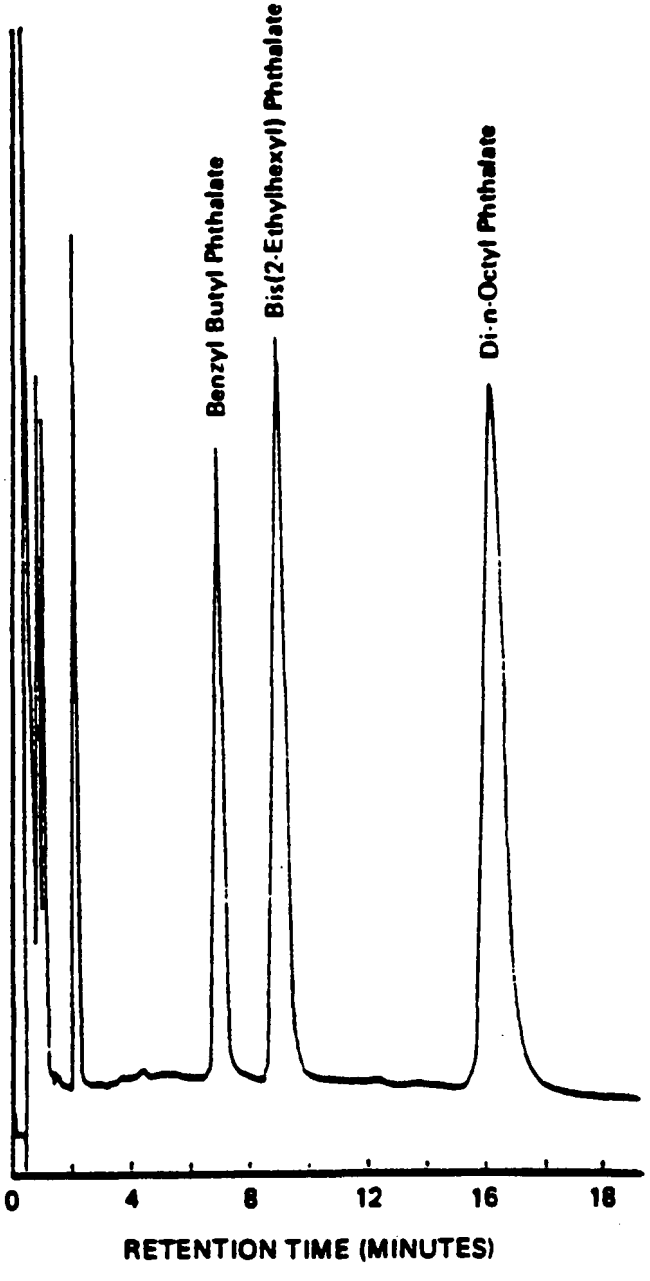


Figure 2. Gas chromatogram of phthalates (example 2).

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, Section 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 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.7 to 106 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 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 1 - Phthalates. Report for EPA Contract 68-03-2606 (in preparation).

2. "Determination of Phthalates in Industrial and Municipal Wastewaters," EPA-600/4-81-063, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, October 1981.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 16, Method 606 (Phthalate Esters)," Report for EPA Contract 68-03-2606 (in preparation).

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.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Bis(2-ethylhexyl)phthalate	50	38.4	1.2-55.9	D-158
Butyl benzyl phthalate	10	4.2	5.7-11.0	30-136
Di-n-butyl phthalate	25	8.9	10.3-29.6	23-136
Diethyl phthalate	25	9.0	1.9-33.4	D-149
Dimethyl phthalate	25	9.5	1.3-35.5	D-156
Di-n-octyl phthalate	50	13.4	D-50.0	D-114

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 606. 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]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Bis(2-ethylhexyl) phthalate	0.53C+2.02	0.80$\bar{X}$-2.56	0.73$\bar{X}$-0.17
Butyl benzyl phthalate	0.82C+0.13	0.26$\bar{X}$+0.04	0.25$\bar{X}$+0.07
Di-n-butyl phthalate	0.79C+0.17	0.23$\bar{X}$+0.20	0.29$\bar{X}$+0.06
Diethyl phthalate	0.70C+0.13	0.27$\bar{X}$+0.05	0.45$\bar{X}$+0.11
Dimethyl phthalate	0.73C+0.17	0.26$\bar{X}$+0.14	0.44$\bar{X}$+0.31
Di-n-octyl phthalate	0.35C-0.71	0.38$\bar{X}$+0.71	0.62$\bar{X}$+0.34

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

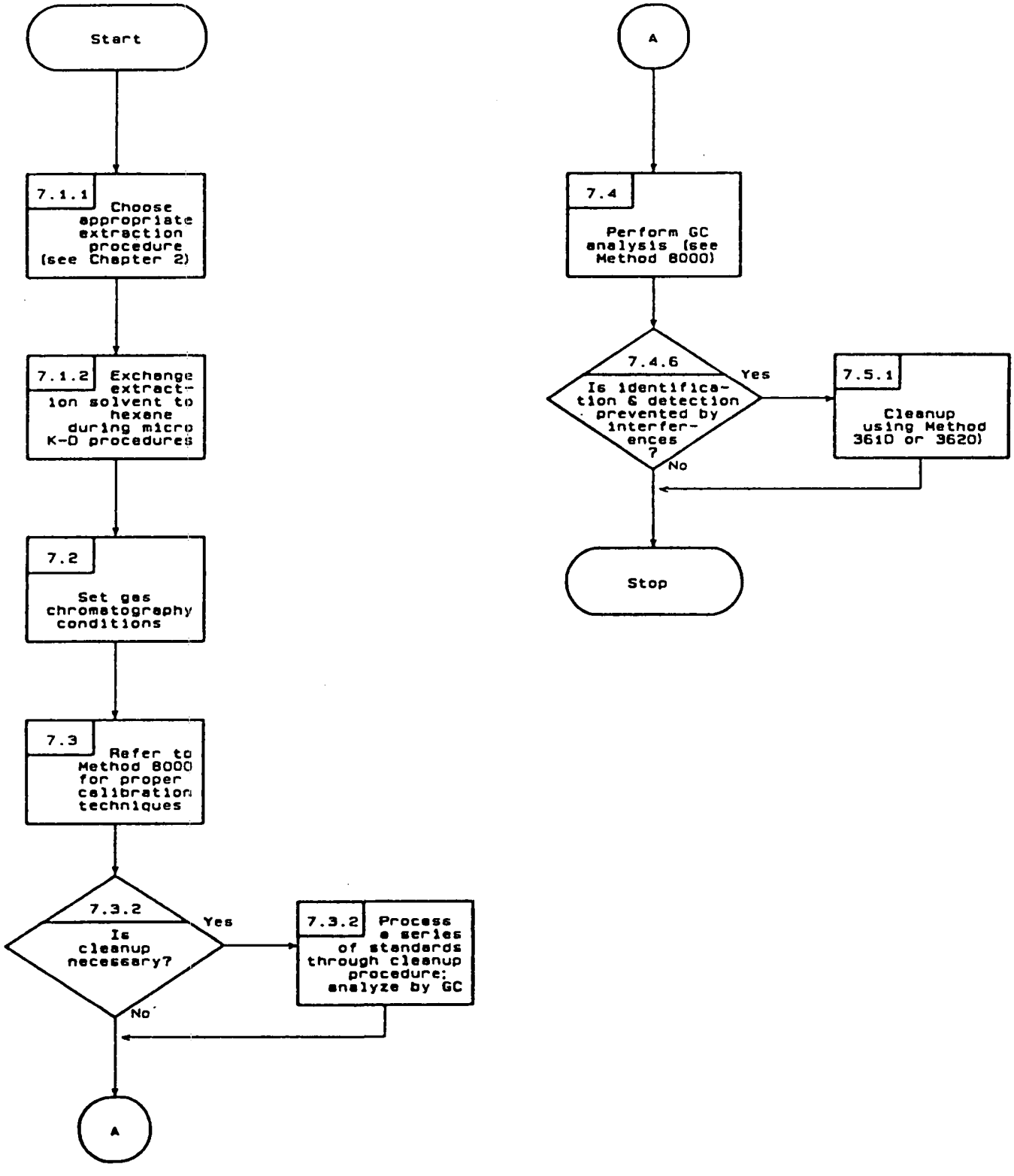
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

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.

[a]Criteria from 40 CFR Part 136 for Method 606.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.6 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3610 or 3620)
No
Stop

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels 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-uL 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 a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level 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 (Section 3.5, in particular), 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.

TABLE 1. GAS CHROMATOGRAPHY OF PESTICIDES AND PCBs[a]

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	Method Detection limit (ug/L)
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

[a]U.S. EPA. Method 617. Organochloride Pesticides and PCBs. Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

e = Multiple peak response.

nd = not determined.

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

[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.

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 I.D. 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 I.D. glass column or equivalent.

4.1.3 **Detectors:** Electron capture (ECD) or halogen specific (HSD) (i.e., electrolytic conductivity detector).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). 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.

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).

4.3 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 (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL 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.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are 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.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 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. Dibutylchlorendate (DBC) is also subject to acid and base degradation. Therefore, two surrogate standards are added to each sample; however, only one need be calculated for recovery. DBC is the primary surrogate and should be used whenever possible. However, if DBC recovery is low or compounds interfere with DBC, then the 2,4,5,6-tetrachloro-meta-xylene should be evaluated for acceptance. Proceed with corrective action when both surrogates are out of limits for a sample (Section 8.3). Method 3500, Section 5.3.2, 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 either Method 3540 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 Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 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:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. 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 so that 4,4'-DDT has a retention time of approximately 12 min.

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-level 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 uL of internal standard to the sample prior to injection.

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-level standard after each group of 10 samples in the analysis sequence.

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 Paragraph 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-level 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 Section 7.7 of Method 8000. Calculate percent breakdown as follows:

$$\% \text{ breakdown for 4,4'-DDT} = \frac{\text{Total DDT degradation peak area (DDE + DDD)}}{\text{Total DDT peak area (DDT + DDE + DDD)}} \times 100$$

$$\% \text{ breakdown for Endrin} = \frac{\text{Total endrin degradation peak area (endrin aldehyde + endrin ketone)}}{\text{Total endrin peak area (endrin + endrin aldehyde + endrin ketone)}} \times 100$$

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 Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

7.6 Calculations (exerpted 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 column 10% DC-200 stationary phase was used to obtain the chromatograms in Figures 6-9.

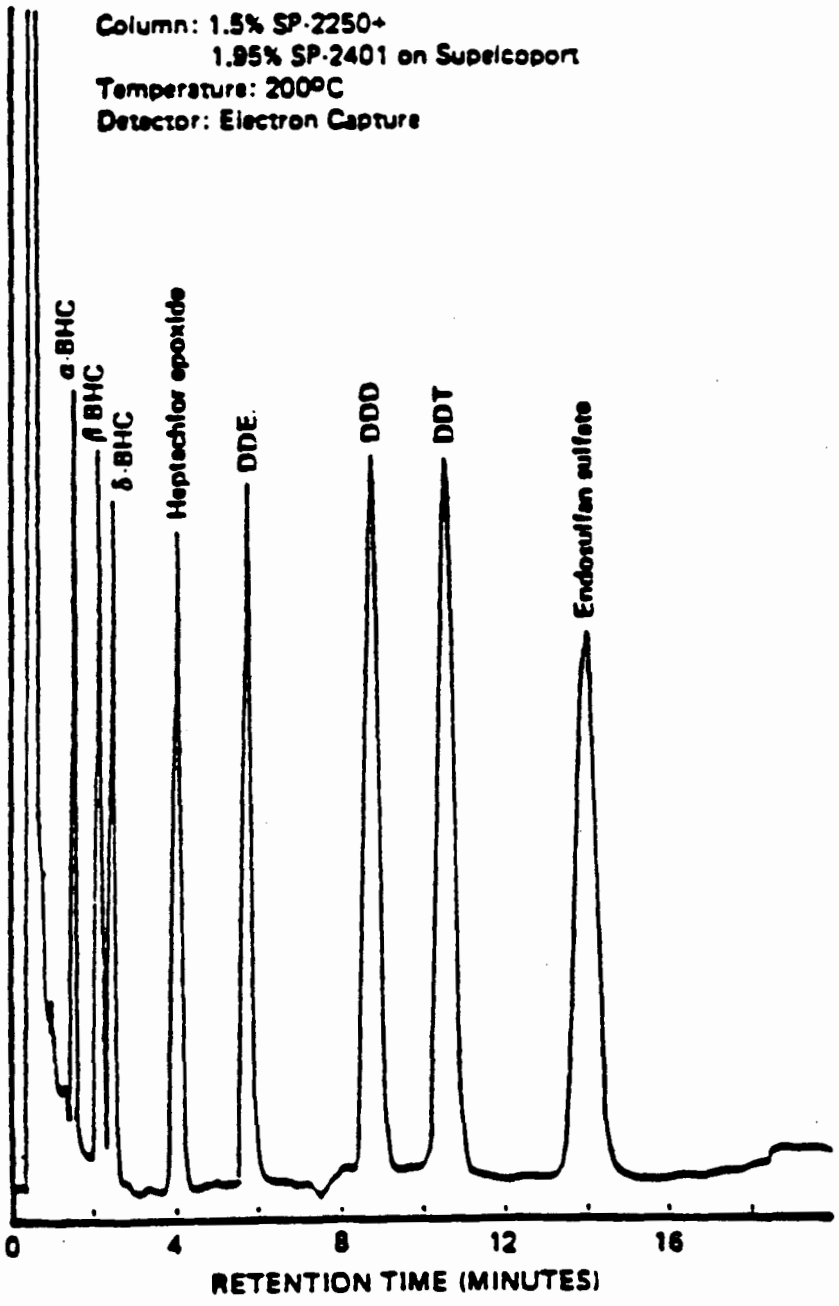


Figure 1. Gas chromatogram of pesticides.

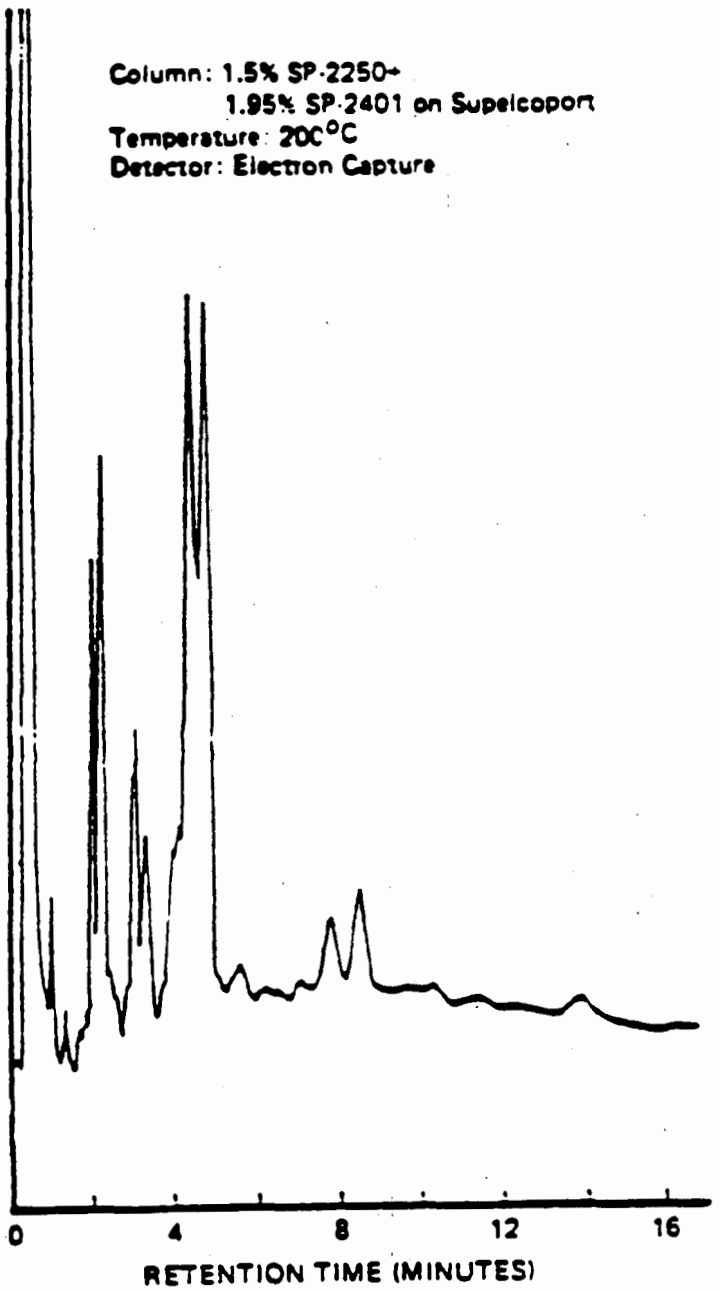


Figure 2. Gas chromatogram of chlordane.

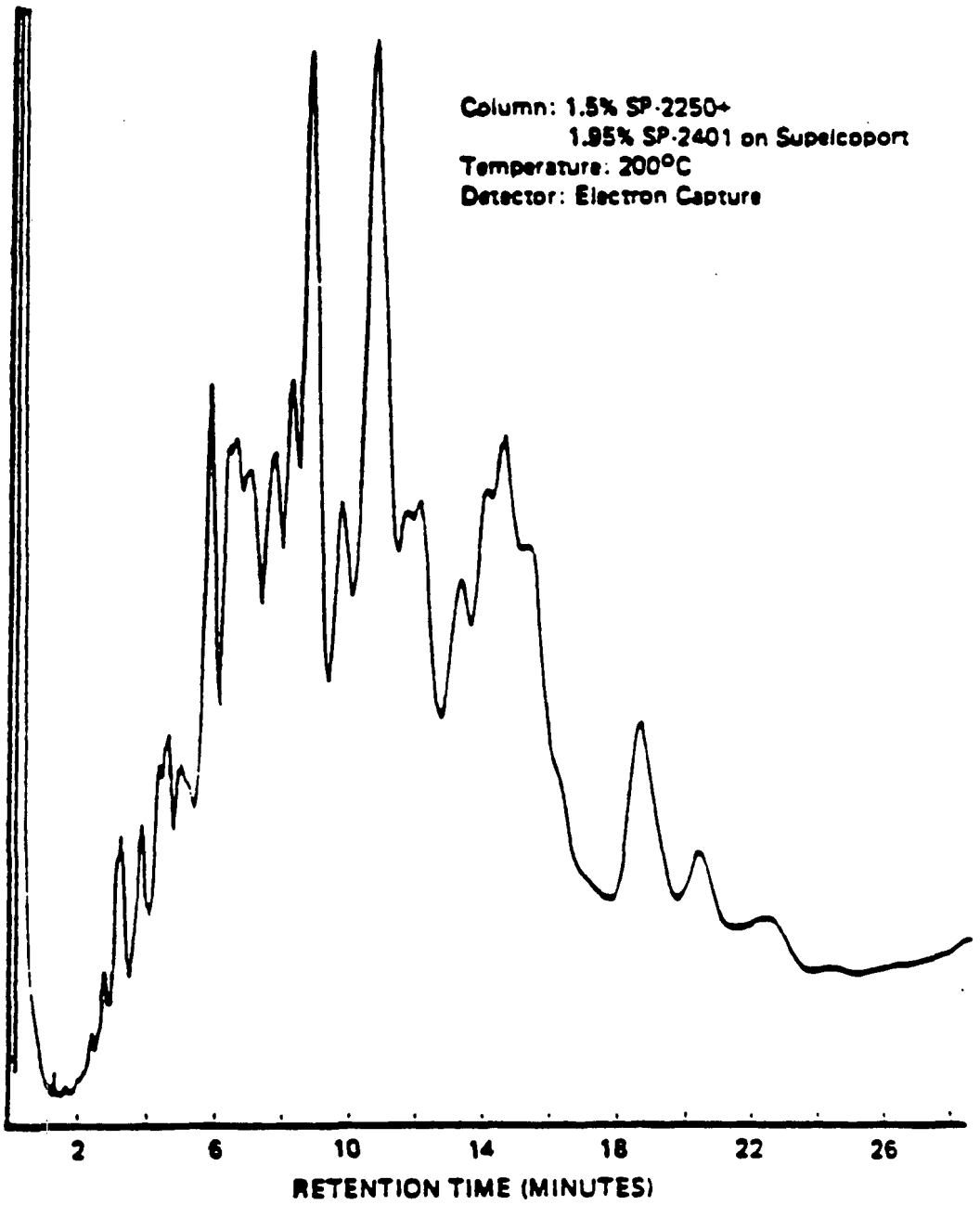


Figure 3. Gas chromatogram of toxaphene.

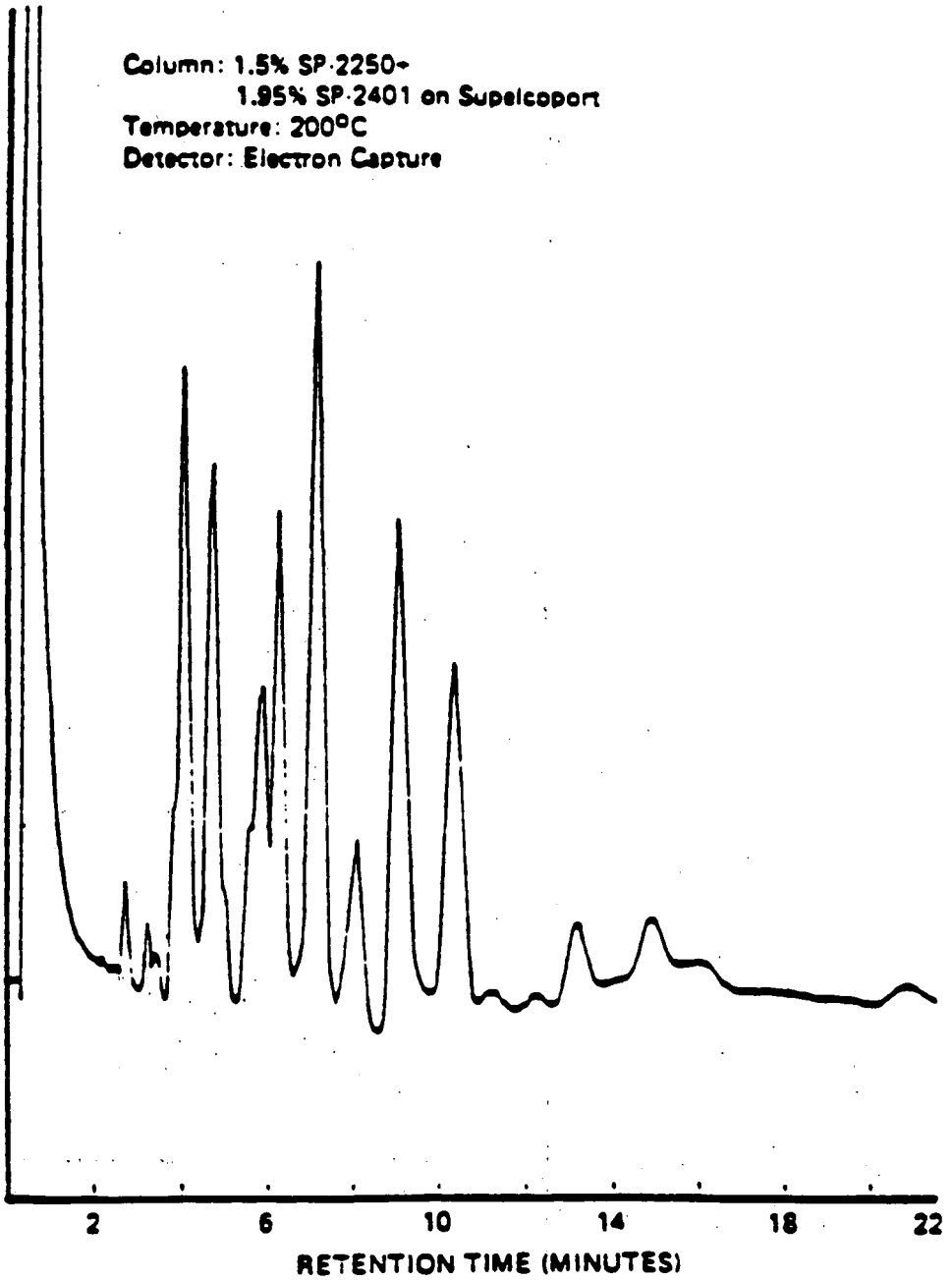


Figure 4. Gas chromatogram of PCB-1254.

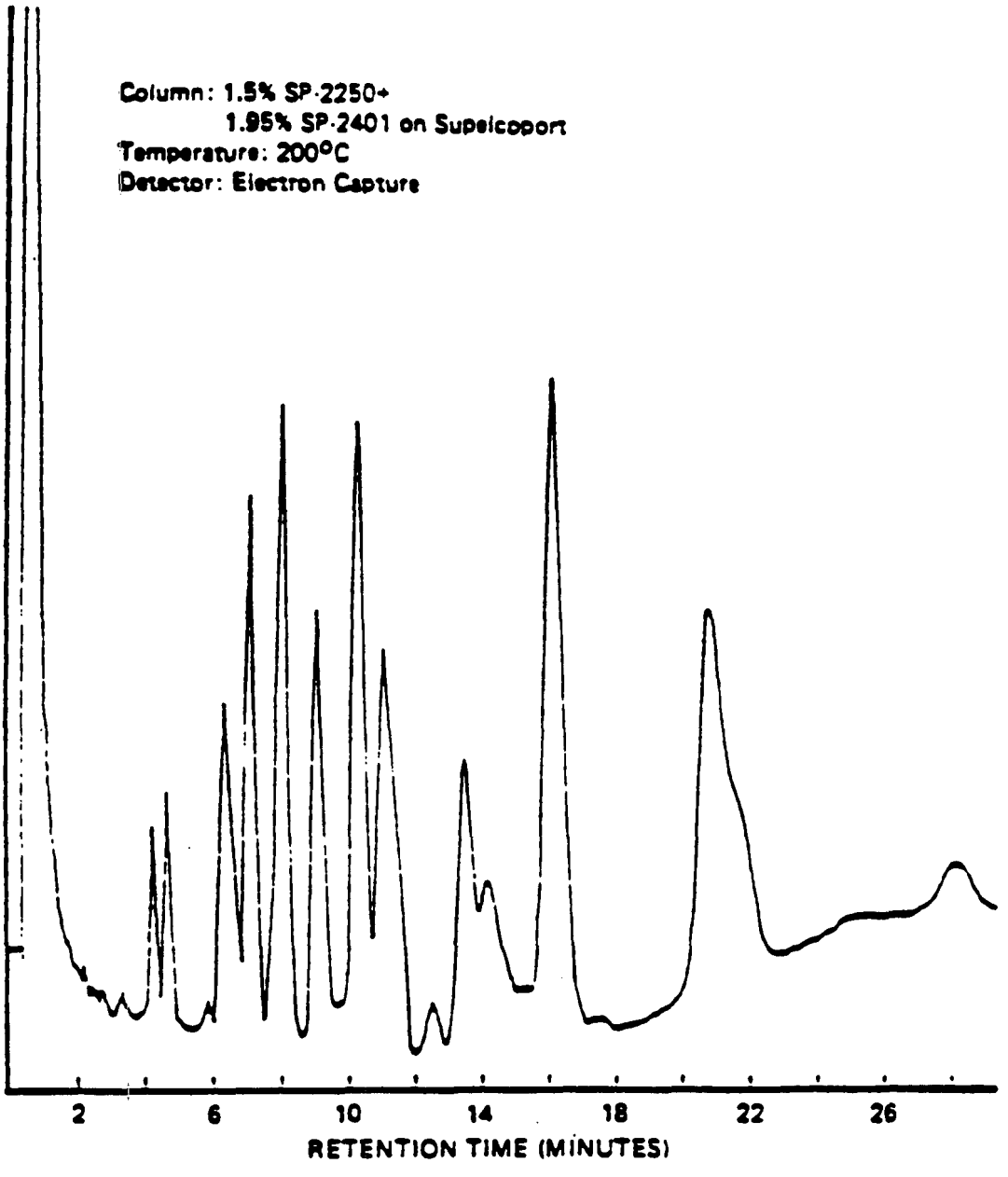


Figure 5. Gas chromatogram of PCB-1260.

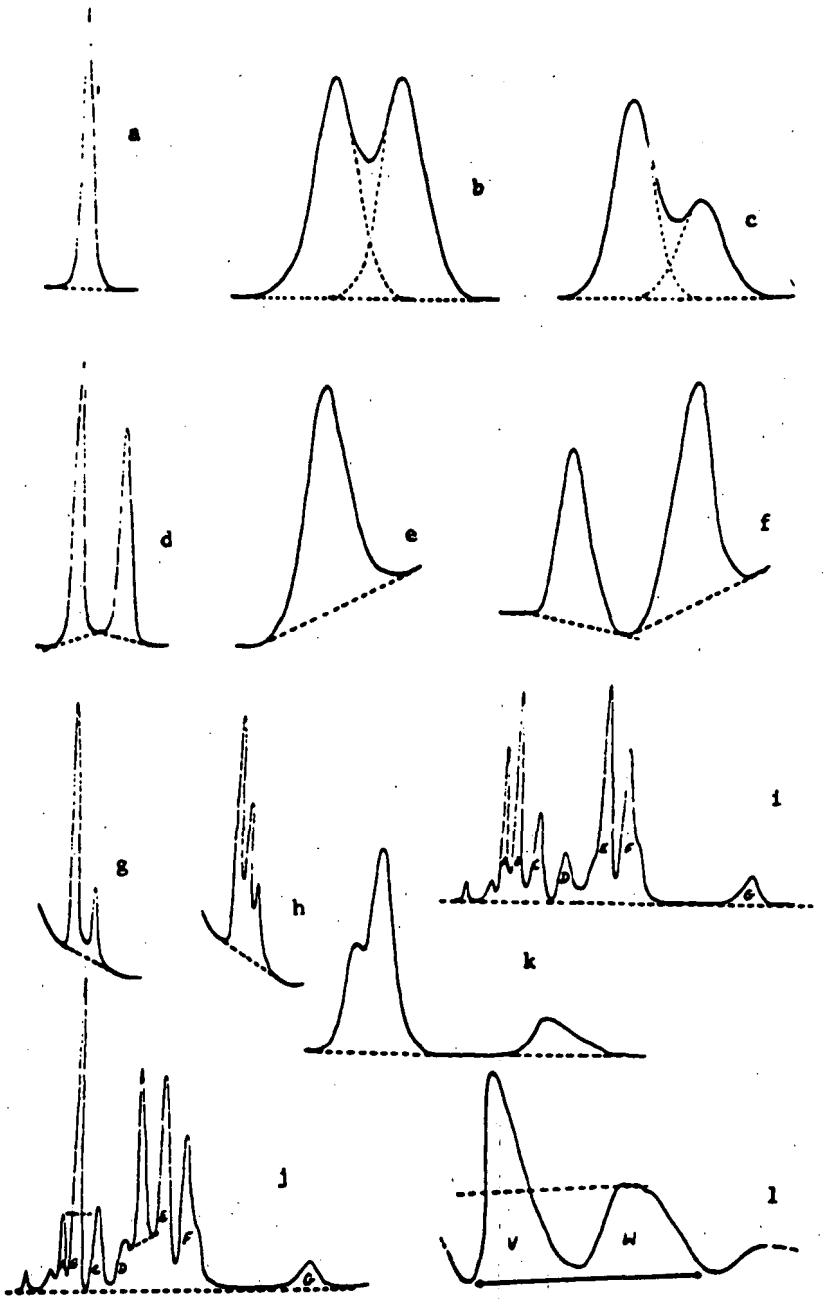


Fig. 6--Baseline construction for some typical gas chromatographic peaks. a, symmetrical separated flat baseline; b and c, overlapping flat baseline; d, separated (pen does not return to baseline between peaks); e, separated sloping baseline; f, separated (pen goes below baseline between peaks); g, α- 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.

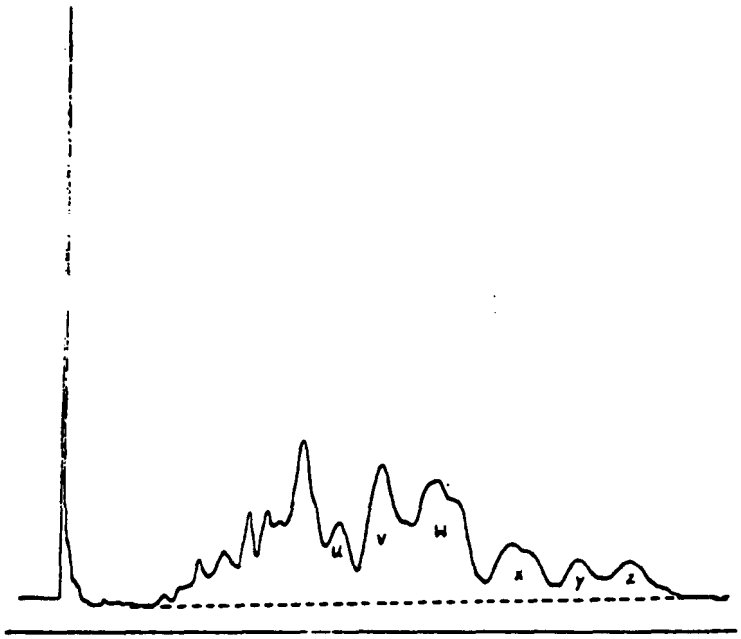


Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

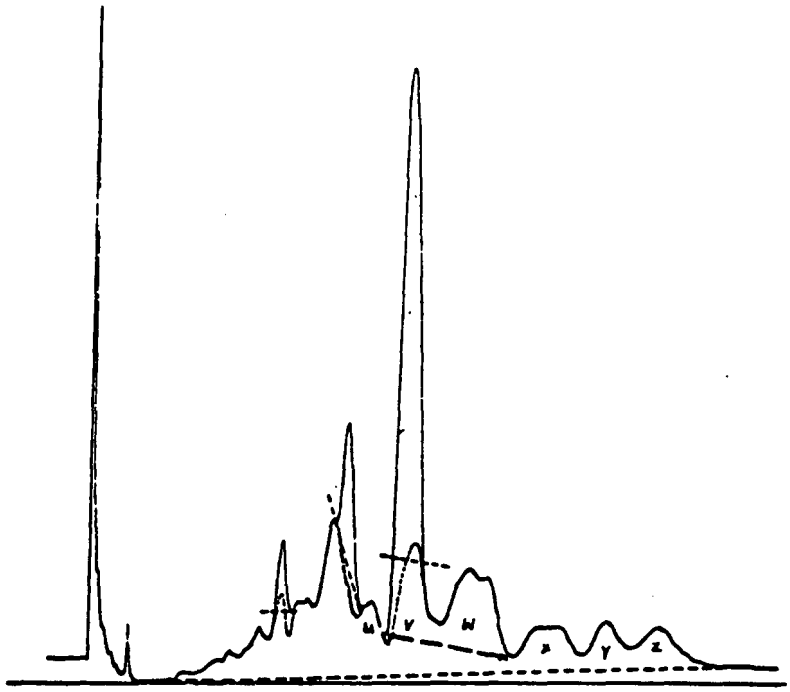


Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

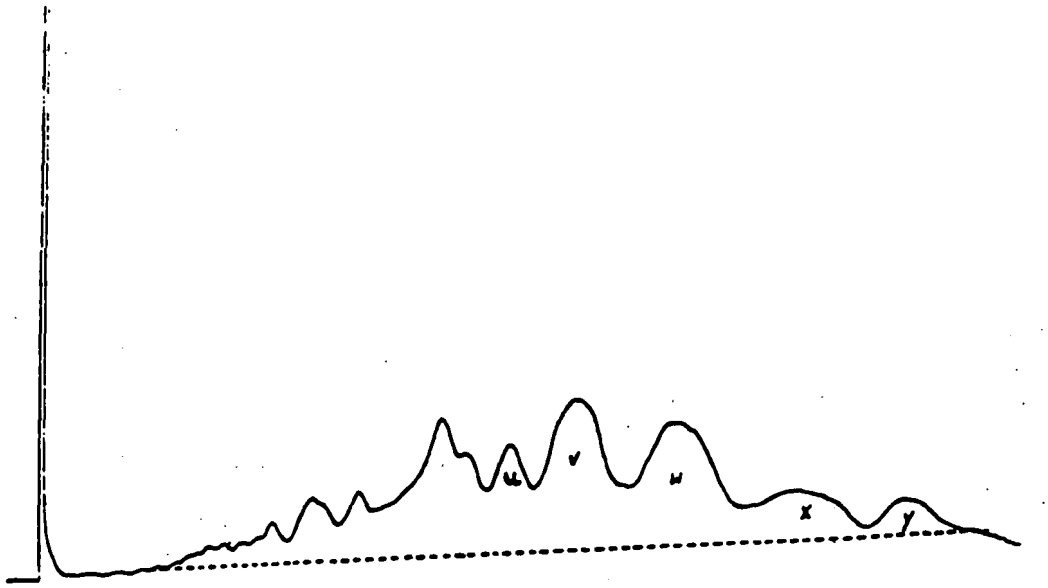


Fig. 8a--Baseline construction for multiple residues: standard toxaphene.

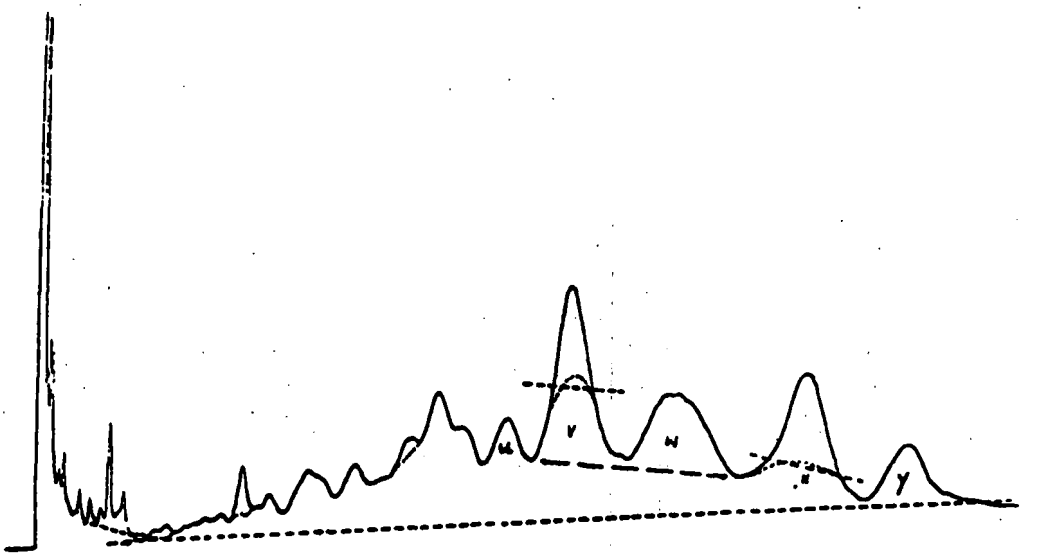


Fig. 8b--Baseline construction for multiple residues: rice bran with BHC, toxaphene, DDT, and methoxychlor.

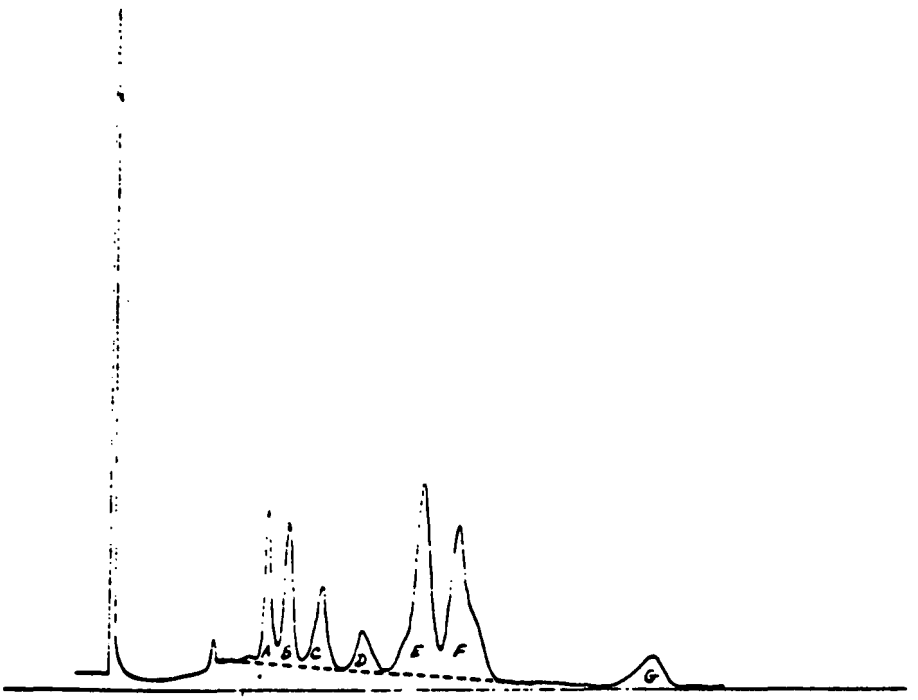


Fig. 9a--Baseline construction for multiple residues: standard chlordane.

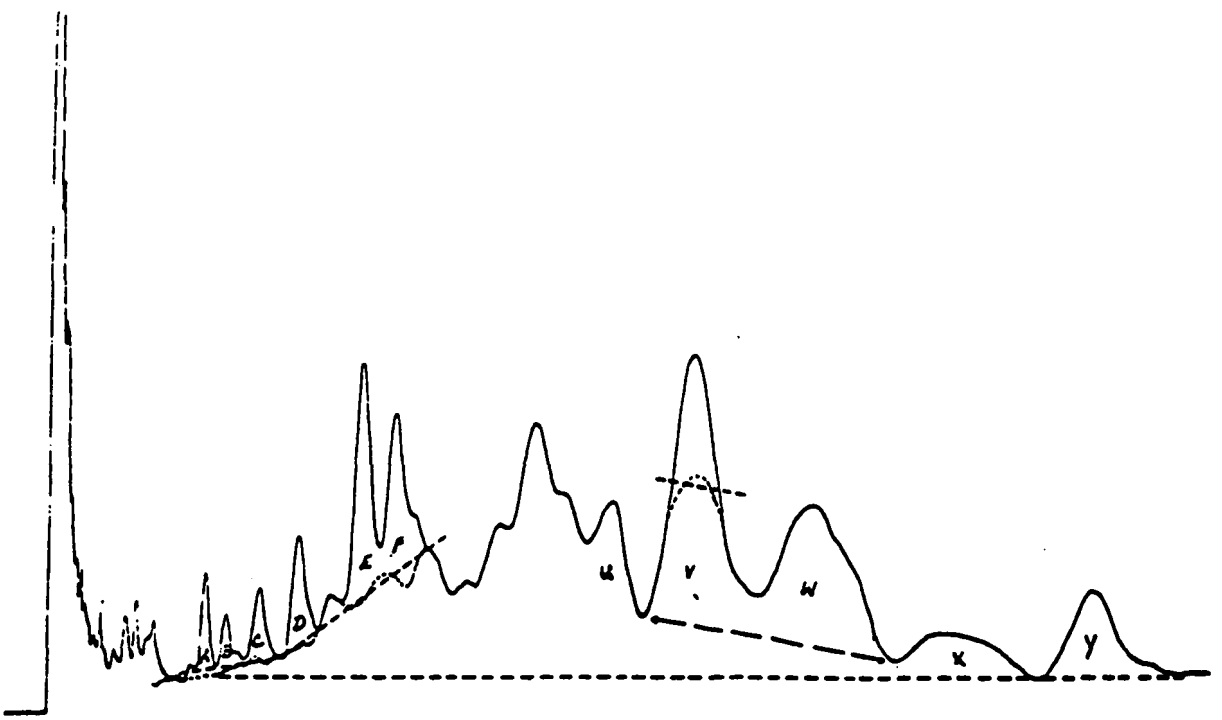


Fig. 9b—Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

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 it 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 metabolities; 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 <u>not</u> 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, 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 and 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 PCB 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 sometime 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 of 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 sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide 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 TDE 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 others 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 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each single-component parameter of interest at the following concentrations in acetone: 4,4'-DDD, 10 ug/mL; 4,4'-DDT, 10 ug/mL; endosulfan II, 10 ug/mL; endosulfan sulfate, 10 ug/mL; endrin, 10ug/mL; and any other single-component pesticide, 2 ug/mL. If this method is only to be used to analyze for PCBs, chlordane, or toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 ug/mL 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, Section 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."

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/uL 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 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 ug/L for single-component pesticides and from 8.5 to 400 ug/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 a flame ionization 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

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

3. Pressley, T.A., and J.E. Longbottom, "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-84-006, 1982.

4. "Determination of Pesticides and PCB's in Industrial and Municipal Wastewaters, U.S. Environmental Protection Agency," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, EPA-600/4-82-023, June 1982.

5. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9, 1971.

6. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

7. Webb, R.G. and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," Journal of Chromatographic Science, 11, 366, 1973.

8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. 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.

10. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

11. U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. 1, June 1979.

12. Sawyer, L.D., JAOAC, 56, 1015-1023 (1973), 61 272-281 (1978), 61 282-291 (1978).

13. Official Methods of Analysis of the Association of Official Analytical Chemists, 12th Edition; Changes in Methods, JAOAC 61, 465-466 (1978), Sec. 29.018.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	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 ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria 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]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/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	0.93C+0.70	0.11$\bar{X}$+1.40	0.21$\bar{X}$+1.52
PCB-1248	0.97C+1.06	0.17$\bar{X}$+0.41	0.25$\bar{X}$-0.37
PCB-1254	0.76C+2.07	0.15$\bar{X}$+1.66	0.17$\bar{X}$+3.62
PCB-1260	0.66C+3.76	0.22$\bar{X}$-2.37	0.39$\bar{X}$-4.86

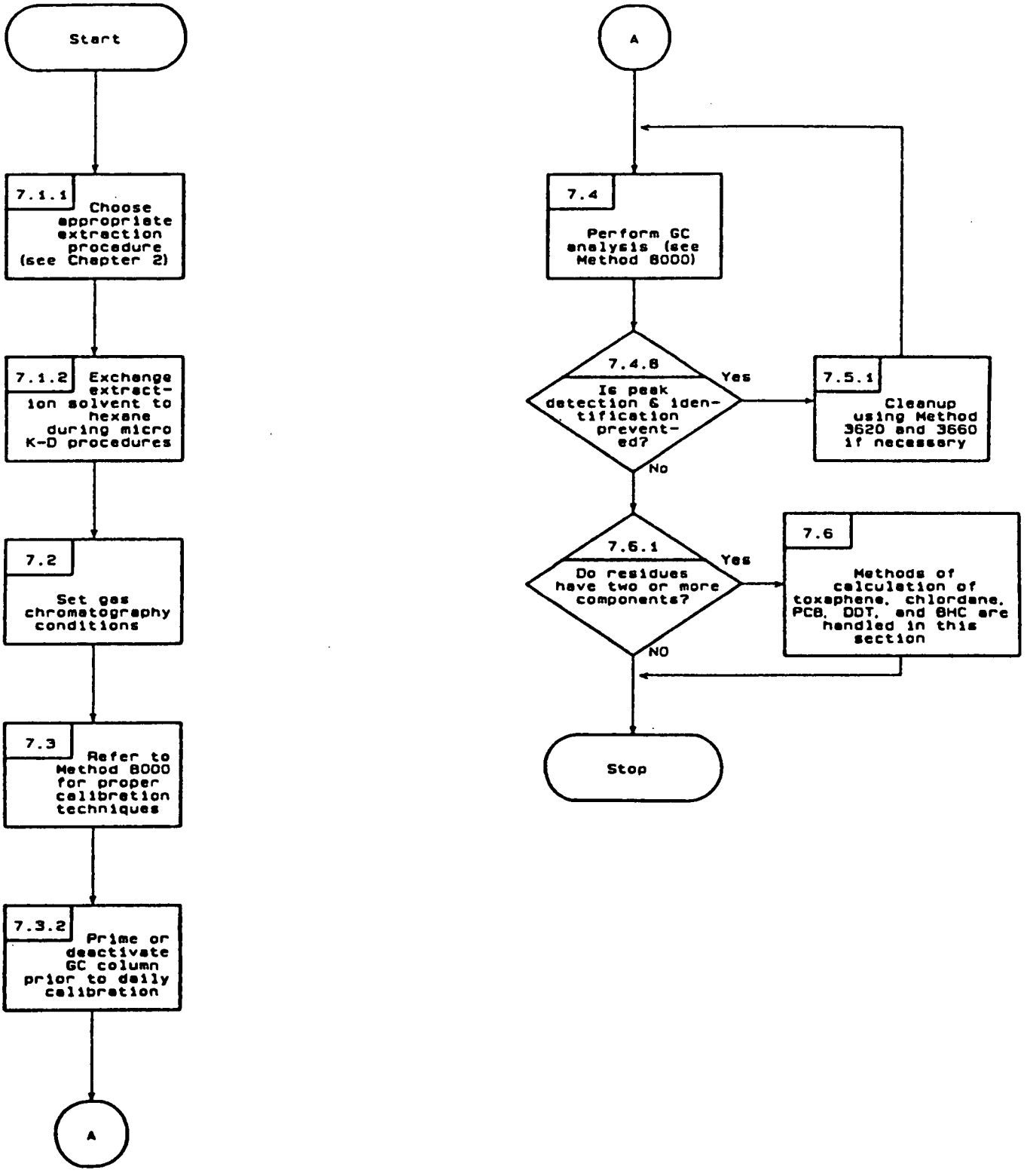
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

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.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Prime or deactivate GC column prior to daily calibration
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.8 Is peak detection & identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary
No
7.6.1 Do residues have two or more components?
Yes
7.6 Methods of calculation of toxaphene, chlordane, PCB, DDT, and BHC are handled in this section
NO
Stop

METHOD 8090

NITROAROMATICS AND CYCLIC KETONES

1.0 SCOPE AND APPLICATION

1.1 Method 8090 is used to determine the concentration of various nitroaromatic and cyclic ketone compounds. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8090 provides gas chromatographic conditions for the detection of ppb levels of nitroaromatic and cyclic ketone compounds. 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 an electron capture detector (ECD) or a flame ionization detector (FID). The dinitrotoluenes are determined using ECD, whereas the other compounds amenable to this method are determined using FID.

2.2 If interferences prevent proper detection of the analytes, the method may also be performed on extracts that have undergone cleanup.

3.0 INTERFERENCES

3.1 Refer to Method 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 of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method 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.

TABLE 1. GAS CHROMATOGRAPHY OF NITROAROMATICS AND ISOPHORONE

Compound	Retention time (min)		Method detection limit (ug/L)	
	Col. 1[a]	Col. 2[b]	ECD	FID
Isophorone	4.49	5.72	15.7	5.7
Nitrobenzene	3.31	4.31	13.7	3.6
2,4-Dinitrotoluene	5.35	6.54	0.02	-
2,6-Dinitrotoluene	3.52	4.75	0.01	-
Dinitrobenzene				
Naphthoquinone				

[a]Column 1: Gas-Chrom Q (80/100 mesh) coated with 1.95% QF-1/1.5% OV-17 packed in a 1.2-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 85°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used when determining the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 145°C.

[b]Column 2: Gas-Chrom Q (80/100 mesh) coated with 3% OV-101 packed in a 3.0-m x 2-mm or 4-mm I.D. glass column. A 2-mm I.D. column and nitrogen carrier gas at 44 mL/min flow rate were used when determining isophorone and nitrobenzene by GC/FID. The column temperature was held isothermal at 100°C. A 4-mm I.D. column and 10% methane/90% argon carrier gas at 44 mL/min flow rate were used to determine the dinitrotoluenes by GC/ECD. The column temperature was held isothermal at 150°C.

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

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]Multiply the Method Detection Limits in Table 1 by the Factor to determine the PQL for each analyte in the matrix to be analyzed.

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 1: 1.2-m x 2- or 4-mm I.D. glass column packed with 1.95% QF-1/1.5% OV-17 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.2.2 Column 2: 3.0-m x 2- or 4-mm I.D. glass column packed with 3% OV-101 on Gas-Chrom Q (80/100 mesh) or equivalent.

4.1.3 **Detectors:** Flame ionization (FID) or electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). 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.

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).

4.3 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 (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: hexane, acetone (pesticide quality or equivalent.)

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in hexane 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.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels are prepared through dilution of the stock standards with hexane. 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 a check standard indicates a problem.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 water blank with one or two surrogates (e.g., 2-fluorobiphenyl) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 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, 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 pH between 5 to 9 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 hexane. The exchange is performed during the K-D procedures listed in all of the extraction methods. The exchange may be performed in one of two ways, depending on the data requirements. If the detection limits cited in Table 1 must be achieved, the exchange should be performed as described starting in Section 7.1.4. If these detection limits are not necessary, solvent exchange is performed as outlined in Section 7.1.3.

7.1.3 **Solvent exchange when detection limits in Table 1 are not required:**

7.1.3.1 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.

7.1.3.2 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. The extract will be handled differently

at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.3.3. If cleanup is needed, proceed to Paragraph 7.1.3.4.

7.1.3.3 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 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 Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis.

7.1.3.4 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 hexane. 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 hexane 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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with 0.2 mL of hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.1.4 **Solvent exchange when detection limits listed in Table 1 must be achieved:**

7.1.4.1 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.

7.1.4.2 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of methylene chloride. A 5-mL syringe is recommended for this operation. Add 1-2 mL of hexane, a clean boiling chip, and attach a two-ball micro-Snyder column. Prewet the column by adding 0.5 mL of hexane to the top. Place the micro-K-D apparatus on the water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete 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 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.4.3 Remove the micro-Snyder column and rinse the flask and its lower joint into the concentrator tube with a minimum amount of hexane. The volume of the extract should be adjusted to 1.0 mL if the extract will be analyzed without cleanup. If the extract will require cleanup, adjust the volume to 2.0 mL with hexane. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with either gas chromatographic analysis or with cleanup, as necessary.

7.2 Gas chromatography conditions (Recommended): The determination of dinitrotoluenes should be performed using GC/ECD. All other compounds amenable to this method are to be analyzed by GC/FID.

7.2.1 **Column 1:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 85°C isothermal. For a 4-mm I.D. column, set the temperature at 145°C isothermal.

7.2.2 **Column 2:** Set 10% methane/90% argon carrier gas flow at 44 mL/min flow rate. For a 2-mm I.D. column, set the temperature at 100°C isothermal. For a 4-mm I.D. column, set the temperature at 150°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 standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.4 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.

7.4 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 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-level standard after each group of 10 samples in the analysis sequence when using FID and after each group of 5 samples in the analysis sequence when using ECD.

7.4.3 An example of a GC/FID chromatogram for nitrobenzene and isophorone is shown in Figure 1. Figure 2 is an example of a GC/ECD chromatogram of the dinitrotoluenes.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Using either the internal or external calibration procedure (Method 8000), determine the identity and quantity of each analyte peak in the sample chromatogram. See Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup:

7.5.1 Proceed with Method 3620, using the 2-mL hexane extracts obtained from either Paragraph 7.1.3.5 or 7.1.4.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

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, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest in acetone at a concentration of 20 ug/mL for each dinitrotoluene and 100 ug/mL for isophorone and nitrobenzene.

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, Section 8.10).

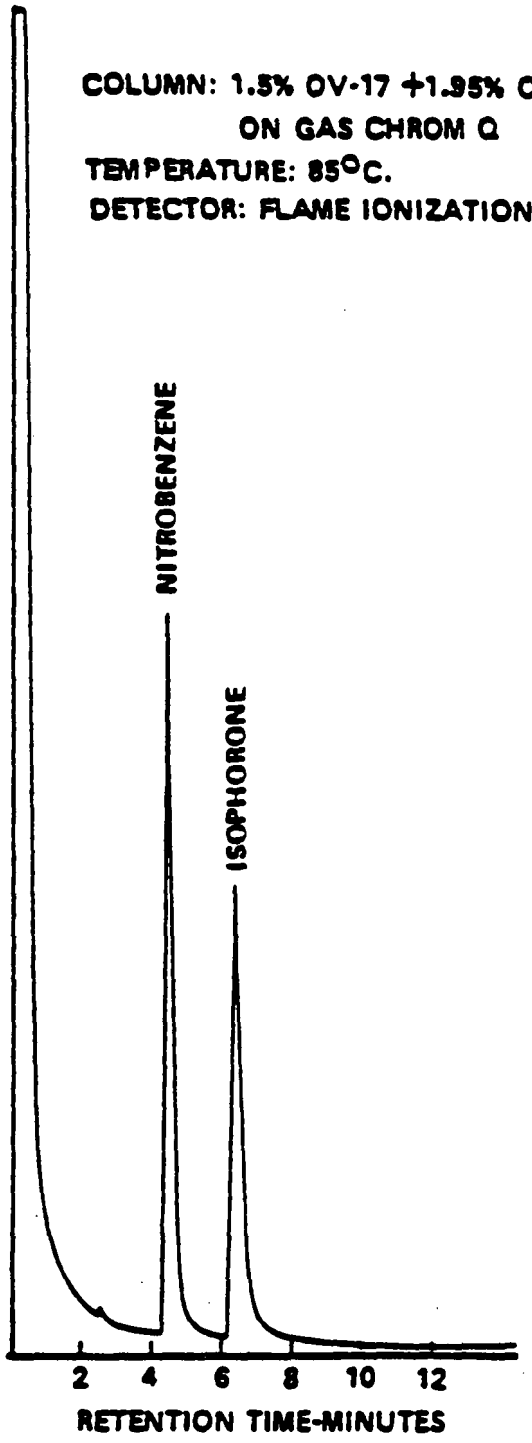


Figure 1. Gas chromatogram of nitrobenzene and isophorone.

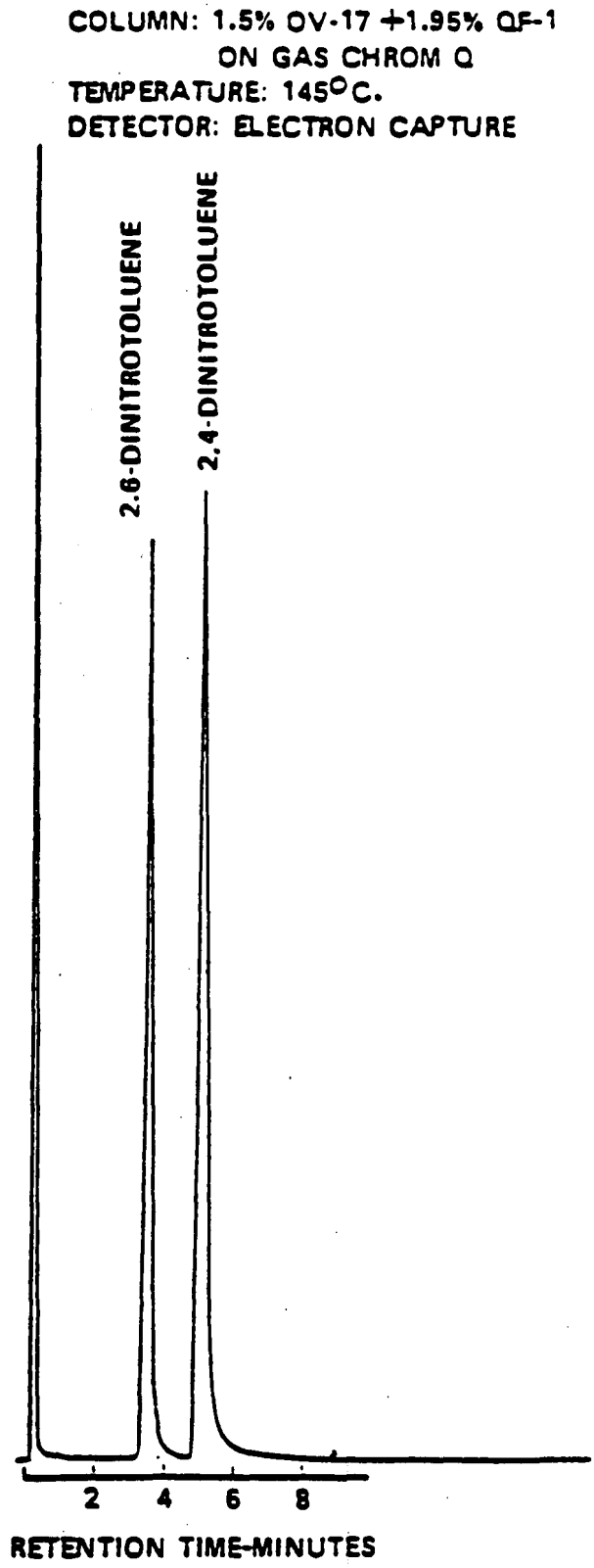


Figure 2. Gas chromatogram of dinitrotoluenes.

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 18 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 515 ug/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 for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 4 - Nitroaromatics and Isophorone,' Report for EPA Contract 68-03-2624 (in preparation).

2. "Determination of Nitroaromatics and Isophorone in Industrial and Municipal Wastewaters," EPA-600/4-82-024, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, June 1982.

3. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. "EPA Method Validation Study 19, Method 609 (Nitroaromatics and Isophorone)," Report for EPA Contract 68-03-2624 (in preparation).

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.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
2,4-Dinitrotoluene	20	5.1	3.6-22.8	6-125
2,6-Dinitrotoluene	20	4.8	3.8-23.0	8-126
Isophorone	100	32.3	8.0-100.0	D-117
Nitrobenzene	100	33.3	25.7-100.0	6-118

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 609. 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

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
2,4-Dinitrotoluene	0.65C+0.22	0.20$\bar{X}$+0.08	0.37$\bar{X}$-0.07
2,4-Dinitrotoluene	0.66C+0.20	0.19$\bar{X}$+0.06	0.36$\bar{X}$-0.00
Isophorene	0.49C+2.93	0.28$\bar{X}$+2.77	0.46$\bar{X}$+0.31
Nitrobenzene	0.60C+2.00	0.25$\bar{X}$+2.53	0.37$\bar{X}$-0.78

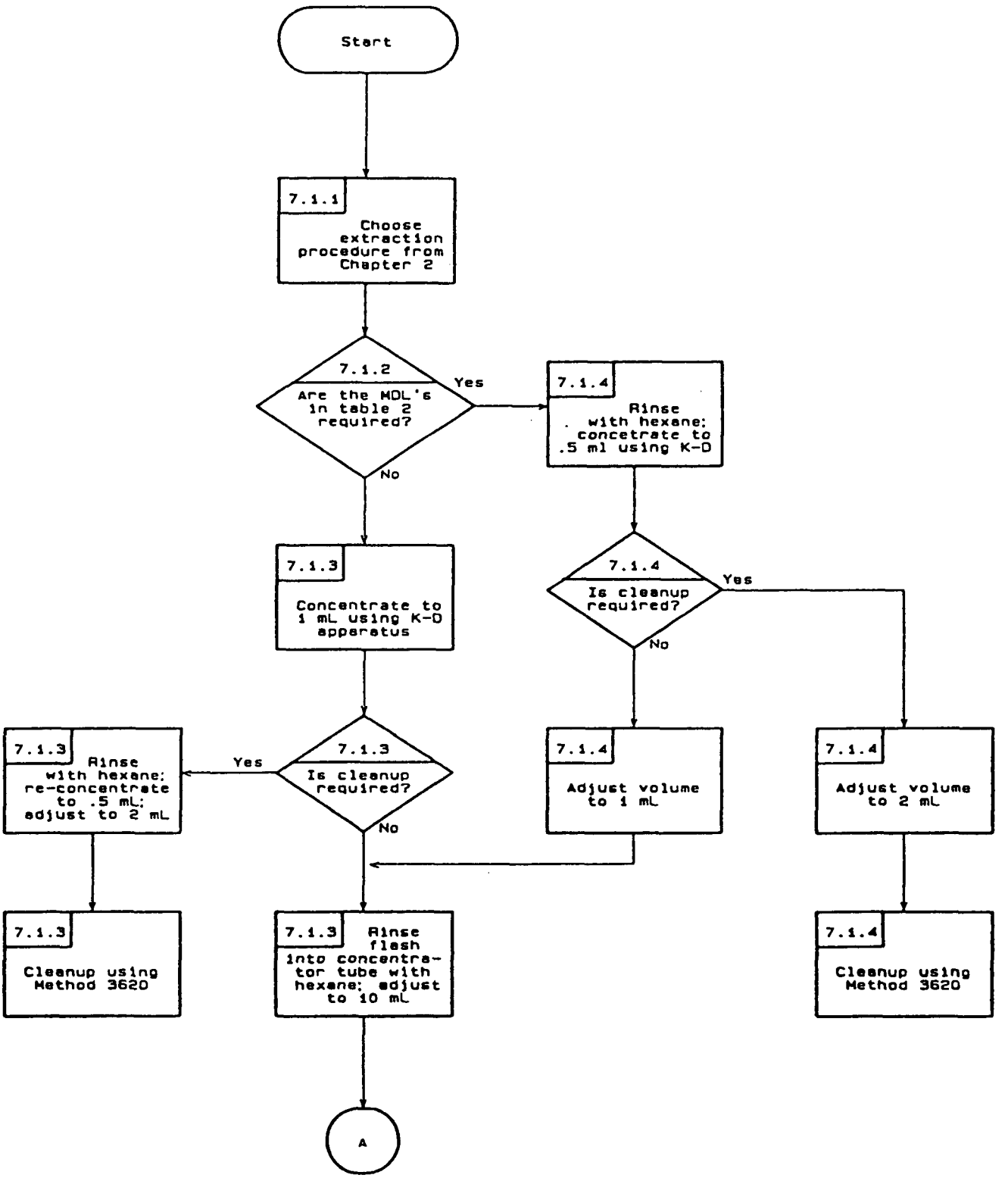
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

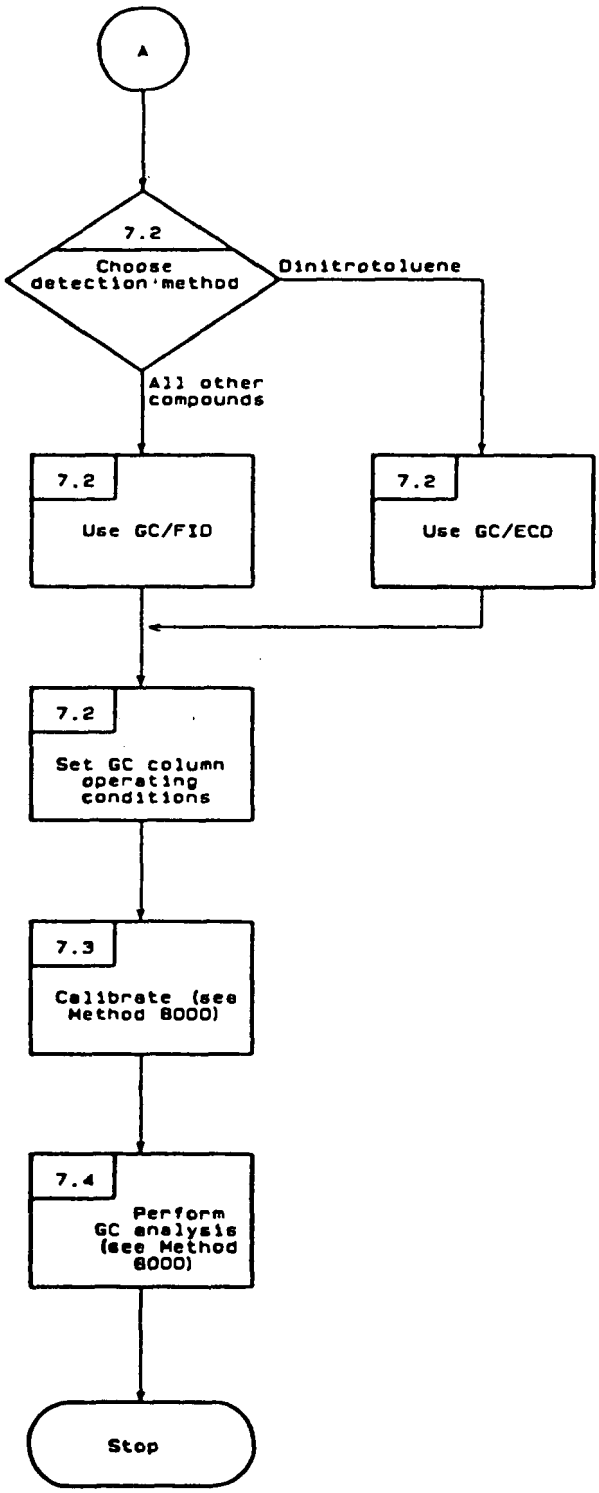
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

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.


Start
7.1.1
Choose extraction procedure from Chapter 2
7.1.2
Are the MDL's in table 2 required?
Yes
No
7.1.4
Rinse with hexane; concetrate to .5 ml using K-D
7.1.3
Concentrate to 1 mL using K-D apparatus
7.1.4
Is cleanup required?
Yes
No
7.1.3
Is cleanup required?
Yes
No
7.1.3
Rinse with hexane; re-concentrate to .5 mL; adjust to 2 mL
7.1.4
Adjust volume to 1 mL
7.1.4
Adjust volume to 2 mL
7.1.3
Cleanup using Method 3620
7.1.3
Rinse flash into concentrator tube with hexane; adjust to 10 mL
7.1.4
Cleanup using Method 3620
A


A
7.2
Choose detection method
Dinitrotoluene
All other compounds
7.2
Use GC/FID
7.2
Use GC/ECD
7.2
Set GC column operating conditions
7.3
Calibrate (see Method 8000)
7.4
Perform GC analysis (see Method 8000)
Stop

METHOD 8100

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8100 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH). Table 1 indicates compounds that may be determined by this method.

1.2 The packed column gas chromatographic method described here cannot adequately resolve the following four pairs of compounds: anthracene and phenanthrene; chrysene and benzo(a)anthracene; benzo(b)fluoranthene and benzo(k)fluoranthene; and dibenzo(a,h)anthracene and indeno(1,2,3-cd)pyrene. The use of a capillary column instead of the packed column, also described in this method, may adequately resolve these PAHs. However, unless the purpose of the analysis can be served by reporting a quantitative sum for an unresolved PAH pair, either liquid chromatography (Method 8310) or gas chromatography/mass spectroscopy (Method 8270) should be used for these compounds.

2.0 SUMMARY OF METHOD

2.1 Method 8100 provides gas chromatographic conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. 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 flame ionization detector (FID).

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

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 of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method 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.

TABLE 1. GAS CHROMATOGRAPHY OF POLYNUCLEAR AROMATIC HYDROCARBONS[a]

Compound	Retention time (min)
Acenaphthene	10.8
Acenaphthylene	10.4
Anthracene	15.9
Benzo(a)anthracene	20.6
Benzo(a)pyrene	29.4
Benzo(b)fluoranthene	28.0
Benzo(j)fluoranthene	
Benzo(k)fluoranthene	28.0
Benzo(ghi)perylene	38.6
Chrysene	24.7
Dibenz(a,h)acridine	
Dibenz(a,j)acridine	
Dibenzo(a,h)anthracene	36.2
7H-Dibenzo(c,g)carbazole	
Dibenzo(a,e)pyrene	
Dibenzo(a,h)pyrene	
Dibenzo(a,i)pyrene	
Fluoranthene	19.8
Fluorene	12.6
Indeno(1,2,3-cd)pyrene	36.2
3-Methylcholanthrene	
Naphthalene	4.5
Phenanthrene	15.9
Pyrene	20.6

[a]Results obtained using Column 1.

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 1: 1.8-m x 2-mm I.D. glass column packed with 3% OV-17 on Chromosorb W-AW-DCMS (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 30-m x 0.25-mm I.D. SE-54 fused silica capillary column.

4.1.2.3 Column 3: 30-m x 0.32-mm I.D. SE-54 fused silica capillary column.

4.1.3 **Detector:** Flame ionization (FID).

4.2 Volumetric flask: 10-, 50-, and 100-mL, ground-glass stopper.

4.3 Microsyringe: 10-uL.

5.0 REAGENTS

5.1 Solvents: Hexane, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane 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.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration 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 a check standard indicates a problem.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 water blank with one or two surrogates (e.g., 2-fluorobiphenyl and 1-fluoronaphthalene) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 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, Section 4.1. Extracts must be stored under refrigeration and must be 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 pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set nitrogen carrier gas flow at 40-mL/min flow rate. Set column temperature at 100°C for 4 min; then program at 8°C/min to a final hold at 280°C.

7.2.2 **Column 2:** Set helium carrier gas at 20-cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 12 min.

7.2.3 **Column 3:** Set helium carrier gas at 60 cm/sec flow rate. Set column temperature at 35°C for 2 min; then program at 10°C/min to 265°C and hold for 3 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques.

7.3.1 The procedure for internal or external standard calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 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 validate elution patterns and the absence of interferents from the reagents.

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 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-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 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 Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the extract may undergo cleanup using Method 3630.

7.5 Cleanup:

7.5.1 Proceed with Method 3630. Instructions are given in this method for exchanging the solvent of the extract to hexane.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

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, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 ug/mL.

8.2.2 Table 2 indicates the calibration and QC acceptance criteria for this method. Table 3 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, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are 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 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 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 3.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (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.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 2. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 3. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Ideno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

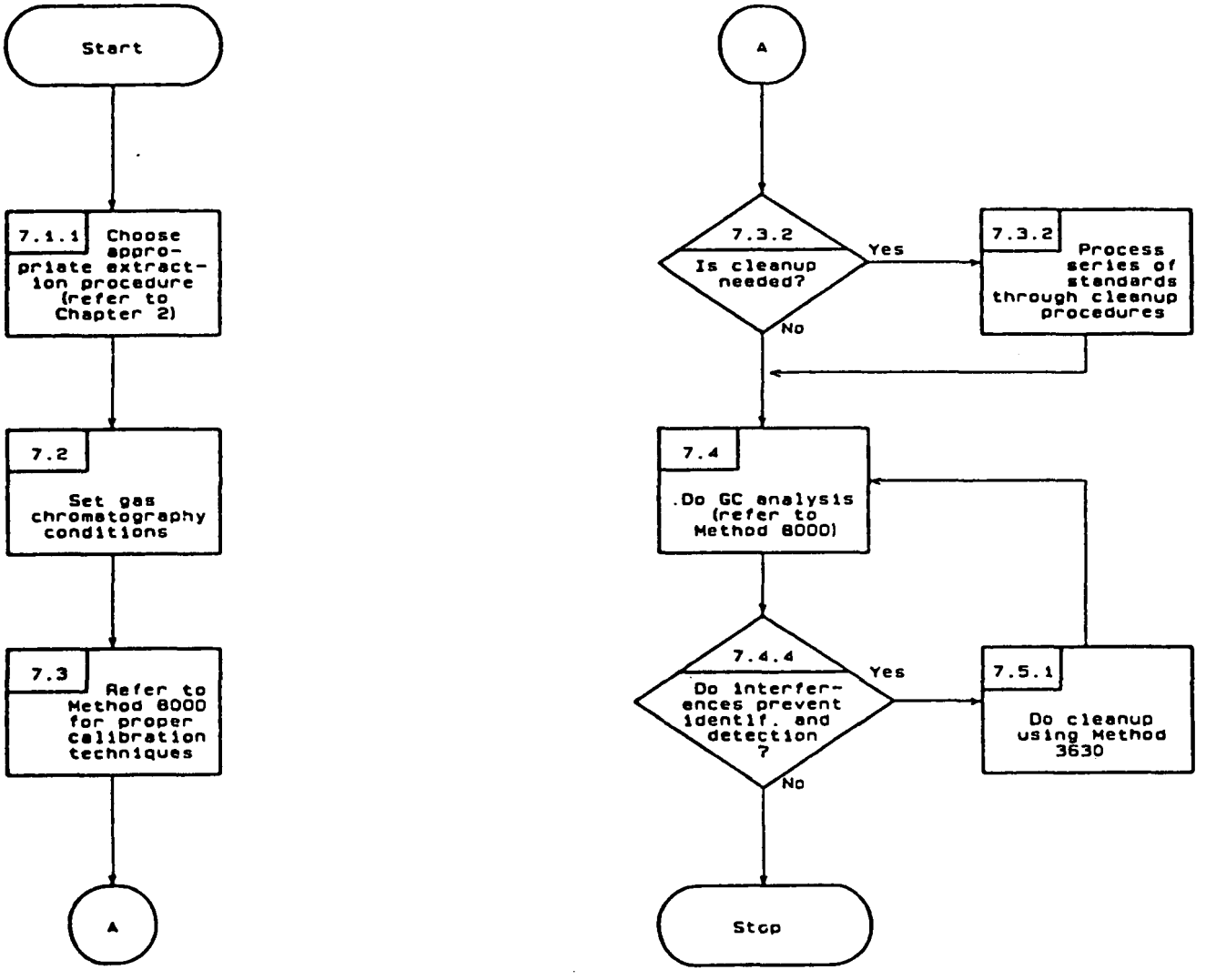
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

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.


Start
7.1.1 Choose appropriate extraction procedure (refer to Chapter 2)
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
A
A
7.3.2 Is cleanup needed?
Yes
No
7.3.2 Process series of standards through cleanup procedures
7.4 Do GC analysis (refer to Method 8000)
7.4.4 Do interferences prevent identif. and detection ?
Yes
No
7.5.1 Do cleanup using Method 3630
Stop

METHOD 8120

CHLORINATED HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8120 is used to determine the concentration of certain chlorinated hydrocarbons. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8120 provides gas chromatographic conditions for the detection of ppb levels of certain chlorinated hydrocarbons. 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 an electron capture detector (ECD).

2.2 If interferences are encountered in the analysis, Method 8120 may also be performed on extracts that have undergone cleanup using Method 3620.

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 of these materials must be demonstrated to be free from interferences, under the conditions of the analysis, by analyzing method 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

TABLE 1. GAS CHROMATOGRAPHY OF CHLORINATED HYDROCARBONS

Compound	Retention time (min) Col. 1	Retention time (min) Col. 2	$	Method Detection limit (ug/L)
Benzal chloride				
Benzotrichloride				
Benzyl chloride				
2-Chloronaphthalene	2.7[a]	3.6[b]		0.94
1,2-Dichlorobenzene	6.6	9.3		1.14
1,3-Dichlorobenzene	4.5	6.8		1.19
1,4-Dichlorobenzene	5.2	7.6		1.34
Hexachlorobenzene	5.6[a]	10.1[b]		0.05
Hexachlorobutadiene	7.7	20.0		0.34
Hexachlorocyclohexane				
Hexachlorocyclopentadiene	nd	16.5[c]		0.40
Hexachloroethane	4.9	8.3		0.03
Tetrachlorobenzenes				
1,2,4-Trichlorobenzene	15.5	22.3		0.05
Pentachlorohexane				

nd = not determined.

[a]150°C column temperature.

[b]165°C column temperature.

[c]100°C column temperature.

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

[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.

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 1: 1.8-m x 2-mm I.D. glass column packed with 1% SP-1000 on Supelcoport (100/120 mesh) or equivalent.

4.1.2.2 Column 2: 1.8-m x 2-mm I.D. glass column packed with 1.5% OV-1/2.4% OV-225 on Supelcoport (80/100 mesh) or equivalent.

4.1.3 **Detector:** Electron capture (ECD).

4.2 Kuderna-Danish (K-D) apparatus:

4.2.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). 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.

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).

4.3 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 (±5°C). The bath should be used in a hood.

4.5 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

4.6 Microsyringe: 10-uL.

4.7 Syringe: 5-mL.

4.8 Vials: Glass, 2-, 10-, and 20-mL capacity with Teflon-lined screw cap.

5.0 REAGENTS

5.1 Solvents: hexane, isooctane, acetone (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane 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.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration 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.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 water blank with one or two surrogates (e.g., chlorinated hydrocarbons that are not expected to be in the sample) recommended to encompass the range of the temperature program used in this method. Method 3500, Section 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, 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 either Method 3540 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 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. The extract will be handled differently at this point, depending on whether or not cleanup is needed. If cleanup is not required, proceed to Paragraph 7.1.2.3. If cleanup is needed, proceed to Paragraph 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 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 Teflon-sealed screw-cap vial. 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 hexane. 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 hexane 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 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

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 hexane. Adjust the extract volume to 2.0 mL and proceed with Method 3620.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 25 mL/min flow rate. Set column temperature at 65°C isothermal, unless otherwise specified (see Table 1).

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 25 mL/min flow rate. Set column temperature at 75°C isothermal, unless otherwise specified (see Table 1).

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 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 validate elution patterns and the absence of interferents from the reagents.

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 injecting.

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-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of GC/ECD chromatograms for certain chlorinated hydrocarbons are shown in Figures 1 and 2.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.4 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 Section 7.8 of Method 8000 for calculation equations.

7.4.5 If peak detection and identification are prevented due to interferences, the hexane extract may undergo cleanup using Method 3620.

7.5 Cleanup:

7.5.1 Proceed with Method 3620 using the 2-mL hexane extracts obtained from Paragraph 7.1.2.5.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

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, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each parameter of interest at the following concentrations in acetone: hexachloro-substituted hydrocarbon, 10 ug/mL; and any other chlorinated hydrocarbon, 100 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, Section 8.10).

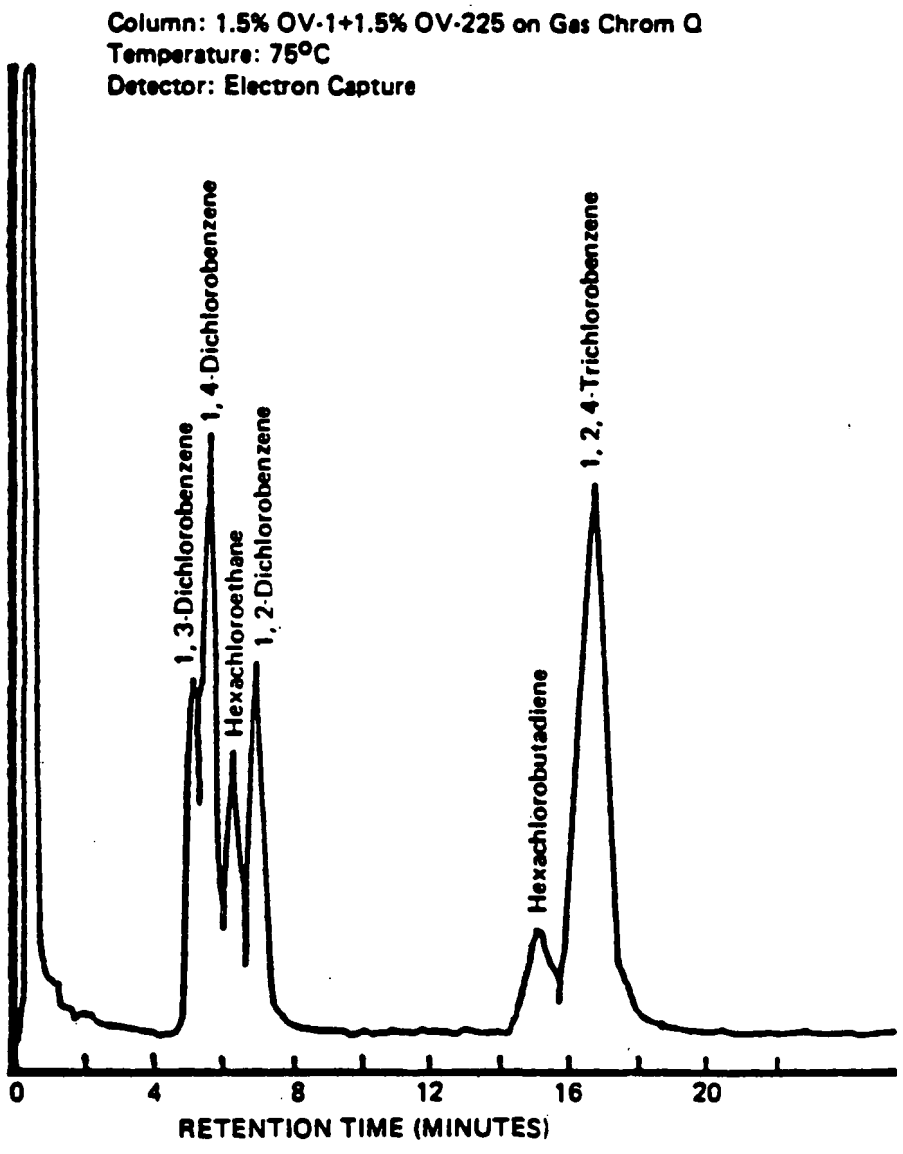


Figure 1. Gas chromatogram of chlorinated hydrocarbons (low molecular weight compounds).

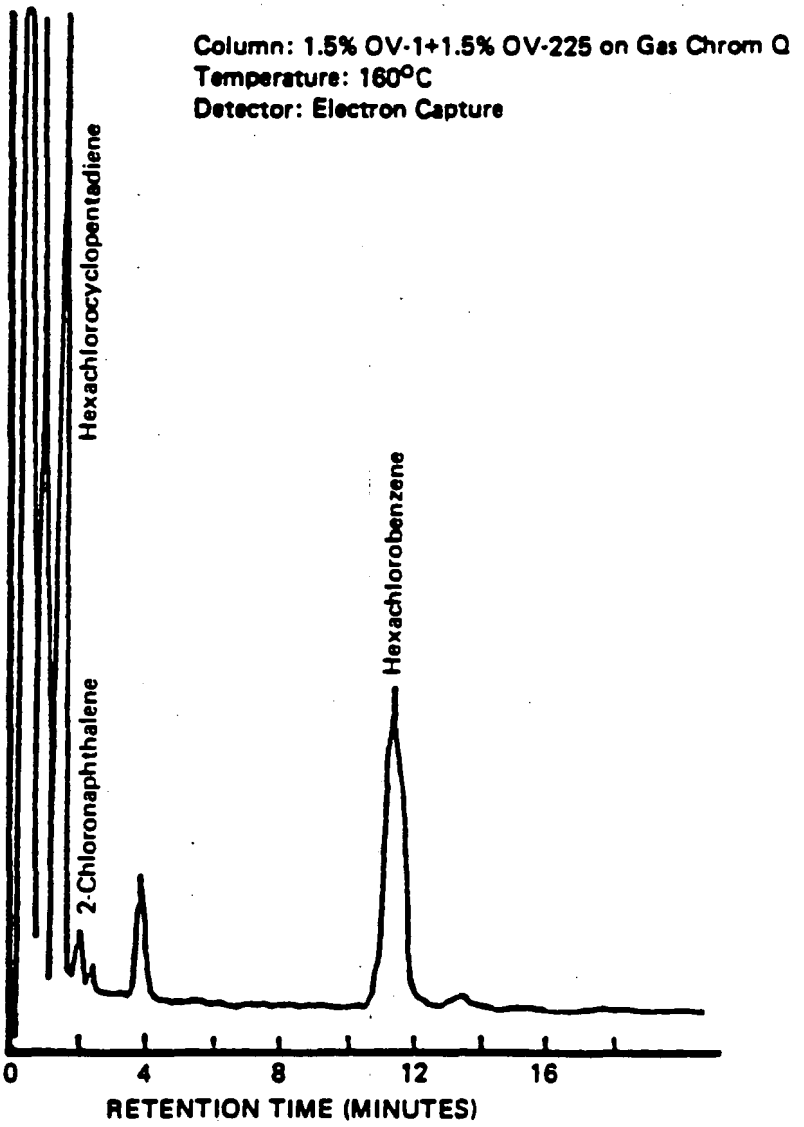


Figure 2. Gas chromatogram of chlorinated hydrocarbons (high molecular weight compounds).

8.3.1 If recovery is not within limits, the following procedures are 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 reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 1.0 to 356 ug/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 for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters. Category 3 - Chlorinated Hydrocarbons, and Category 8 - Phenols," Report for EPA Contract 68-03-2625 (in preparation).

2. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

3. "EPA Method Validation Study 22, Method 612 (Chlorinated Hydrocarbons)," Report for EPA Contract 68-03-2625 (in preparation).

4. "Method Performance for Hexachlorocyclopentadiene by Method 612," Memorandum from R. Slater, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, December 7, 1983.

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. "Determination of Chlorinated Hydrocarbons in Industrial and Municipal Wastewaters," Report for EPA Contract 68-03-2625 (in preparation).

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_s (%)
2-Chloronaphthalene	100	37.3	29.5-126.9	9-148
1,2-Dichlorobenzene	100	28.3	23.5-145.1	9-160
1,3-Dichlorobenzene	100	26.4	7.2-138.6	D-150
1,4-Dichlorobenzene	100	20.8	22.7-126.9	13-137
Hexachlorobenzene	10	2.4	2.6-14.8	15-159
Hexachlorobutadiene	10	2.2	D-12.7	D-139
Hexachlorocyclopentadiene	10	2.5	D-10.4	D-111
Hexachloroethane	10	3.3	2.4-12.3	8-139
1,2,4-Trichlorobenzene	100	31.6	20.2-133.7	5-149

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 612. 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]

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Chloronaphthalene	0.75C+3.21	0.28$\bar{X}$-1.17	0.38$\bar{X}$-1.39
1,2-Dichlorobenzene	0.85C-0.70	0.22$\bar{X}$-2.95	0.41$\bar{X}$-3.92
1,3-Dichlorobenzene	0.72C+0.87	0.21$\bar{X}$-1.03	0.49$\bar{X}$-3.98
1,4-Dichlorobenzene	0.72C+2.80	0.16$\bar{X}$-0.48	0.35$\bar{X}$-0.57
Hexachlorobenzene	0.87C-0.02	0.14$\bar{X}$+0.07	0.36$\bar{X}$-0.19
Hexachlorobutadiene	0.61C+0.03	0.18$\bar{X}$+0.08	0.53$\bar{X}$-0.12
Hexachlorocyclopentadiene[a]	0.47C	0.24$\bar{X}$	0.50$\bar{X}$
Hexachloroethane	0.74C-0.02	0.23$\bar{X}$+0.07	0.36$\bar{X}$-0.00
1,2,4-Trichlorobenzene	0.76C+0.98	0.23$\bar{X}$-0.44	0.40$\bar{X}$-1.37

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

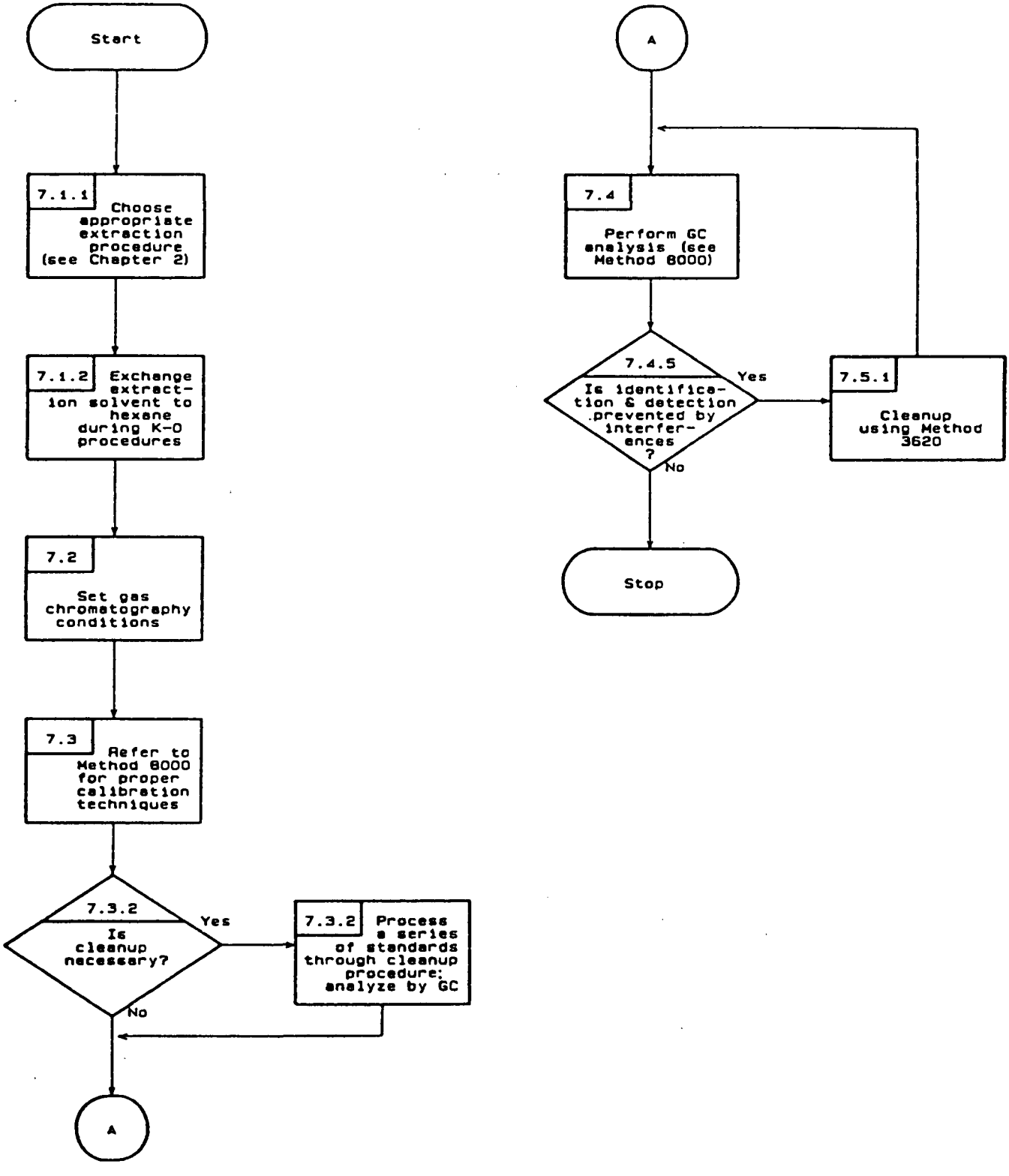
s_r' = Expected single analyst standard deviation of measurements at an average concentration of $\bar{X}$, in ug/L.

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.

[a]Estimates based upon the performance in a single laboratory.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3620
No
Stop

METHOD 8140

ORGANOPHOSPHORUS PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8140 is a gas chromatographic (GC) method used to determine the concentration of various organosphosphorus pesticides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative techniques if mass spectroscopy is not employed. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2.0 SUMMARY OF METHOD

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to analysis, 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, and compounds in the GC effluent are detected with a flame photometric or thermionic detector.

2.2 If interferences are encountered in the analysis, Method 8140 may also be performed on extracts that have undergone cleanup using Method 3620 and/or Method 3660.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 The use of Florisil cleanup materials (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorous pesticides as a function of Florisil fractions. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

TABLE 1. GAS CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS FOR ORGANOPHOSPHOROUS PESTICIDES[a]

Compound	GC column[b]	Retention time (min)	Method detection limit (ug/L)
Azinphos methyl	1a	6.80	1.5
Bolstar	1a	4.23	0.15
Chlorpyrifos	2	6.16	0.3
Coumaphos	1a	11.6	1.5
Demeton-O	1a	2.53	0.25
Demeton-S	1a	1.16	0.25
Diazinon	2	7.73	0.6
Dichlorvos	1b, 3	0.8, 1.50	0.1
Disulfoton	1a	2.10	0.20
Ethoprop	2	3.02	0.25
Fensulfothion	1a	6.41	1.5
Fenthion	1a	3.12	0.10
Merphos	2	7.45	0.25
Mevinphos	1b	2.41	0.3
Naled	3	3.28	0.1
Parathion methyl	2	3.37	0.03
Phorate	1a	1.43	0.15
Ronnel	2	5.57	0.3
Stirophos (Tetrachlorvinphos)	1b, 3	8.52, 5.51	5.0
Tokuthion (Prothiofos)	1a	3.40	0.5
Trichloronate	1a	2.94	0.15

[a]Development of Analytical Test Procedures for Organic Pollutants in Wastewater; Report for EPA Contract 68-03-2711 (in preparation).

[b]See Sections 4.2.1 and 7.2 for column descriptions and conditions.

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

[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.

3.3 Use of a flame photometric detector in the phosphorus mode will minimize interferences from materials that do not contain phosphorus. Elemental sulfur, however, may interfere with the determination of certain organophosphorus pesticides by flame photometric gas chromatography. Sulfur cleanup using Method 3660 may alleviate this interference.

3.4 A halogen-specific detector (i.e., electrolytic conductivity or microcoulometric) is very selective for the halogen-containing pesticides and is recommended for use with dichlorvos, naled, and stirophos.

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 areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 2-mm I.D. glass, packed with 5% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.2 Column 2: 1.8-m x 2-mm I.D. glass, packed with 3% SP-2401 on Supelcoport, 100/120 mesh (or equivalent).

4.1.1.3 Column 3: 50-cm x 1/8-in O.D. Teflon, packed with 15% SE-54 on Gas Chrom Q, 100/120 mesh (or equivalent).

4.1.2 **Detectors:** The following detectors have proven effective in analysis for the analytes listed in Table 1 and were used to develop the accuracy and precision statements in Section 9.0.

4.1.2.1 Phosphorus-specific: Nitrogen/Phosphorus (N/P), operated in phosphorus-sensitive mode.

4.1.2.2 Flame Photometric (FPD): FPD is more selective for phosphorus than the N/P.

4.1.2.3 Halogen-specific: Electrolytic conductivity or microcoulometric. These are very selective for those pesticides containing halogen substituents.

4.2 Balance: analytical, capable of accurately weighing to the nearest 0.0001 g.

4.3 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw-cap.

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 (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

4.9 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest 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 standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.4 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.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with hexane or other suitable solvent.

5.4.3 Analyze each calibration standard according to Section 7.0.

5.5 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 water blank with one or two surrogates (e.g., organophosphorous pesticides not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. 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, 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 either Method 3540 or 3550.

7.1.2 Prior to gas chromatographic analysis, the extraction solvent may be exchanged to hexane. This is recommended if the detector used is halogen-specific. 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 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 Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1a:** Set helium carrier gas flow at 30 mL/min flow rate. Column temperature is set at 150°C for 1 min and then programmed at 25°C/min to 220°C and held.

7.2.2 **Column 1b:** Set nitrogen carrier gas flow at 30 mL/min flow rate. Column temperature is set at 170°C for 2 min and then programmed at 20°C/min to 220°C and held.

7.2.3 **Column 2:** Set helium carrier gas at 25 mL/min flow rate. Column temperature is set at 170°C for 7 min and then programmed at 10°C/min to 250°C and held.

7.2.4 **Column 3:** Set nitrogen carrier gas at 30 mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 25°C/min to 200°C and held.

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 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.

7.4 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 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-level standard after each group of 10 samples in the analysis sequence.

7.4.3 Examples of chromatograms for various organophosphorous pesticides are shown in Figures 1 through 4.

7.4.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.4.5 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 Section 7.8 of Method 8000 for calculation equations.

7.4.6 If peak detection and identification are prevented due to interferences, the hexane extract may 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 Paragraph 7.1.2.3.

7.5.2 Following cleanup, the extracts should be analyzed by GC, as described in the previous paragraphs and in Method 8000.

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, Section 8.6.

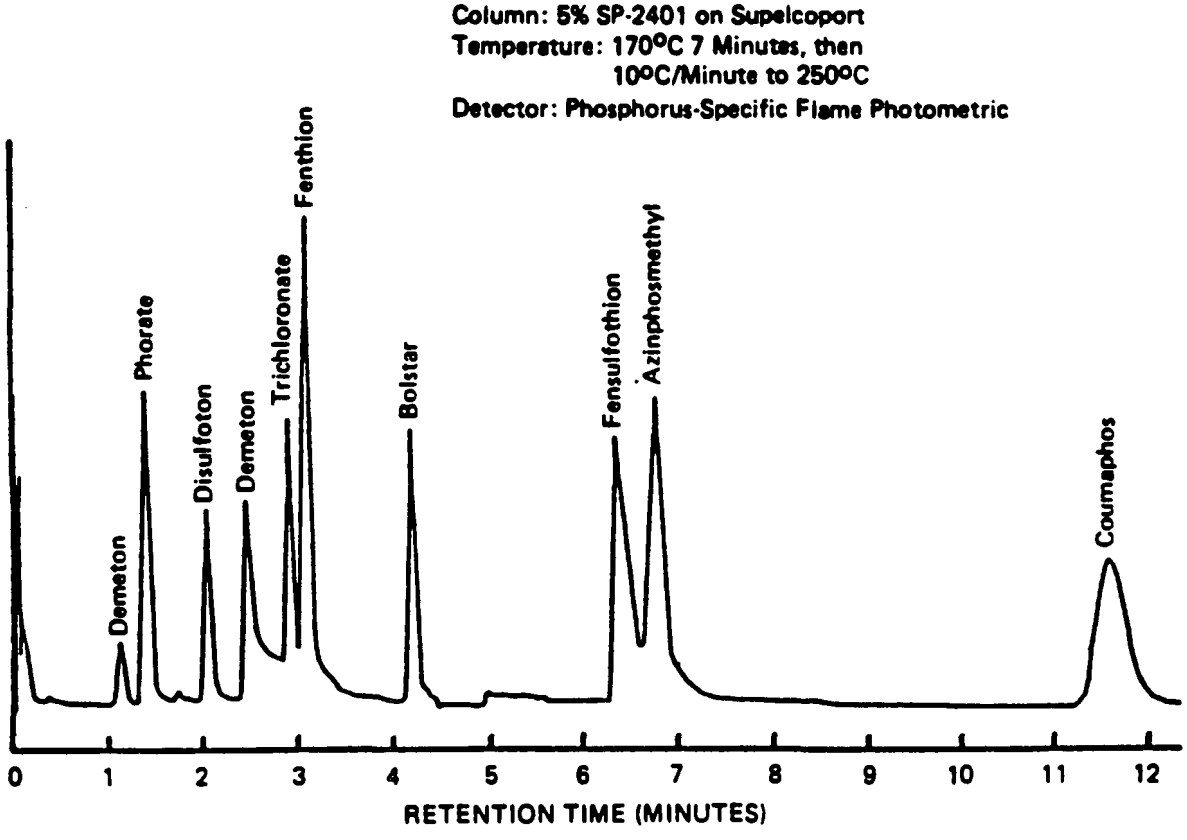


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

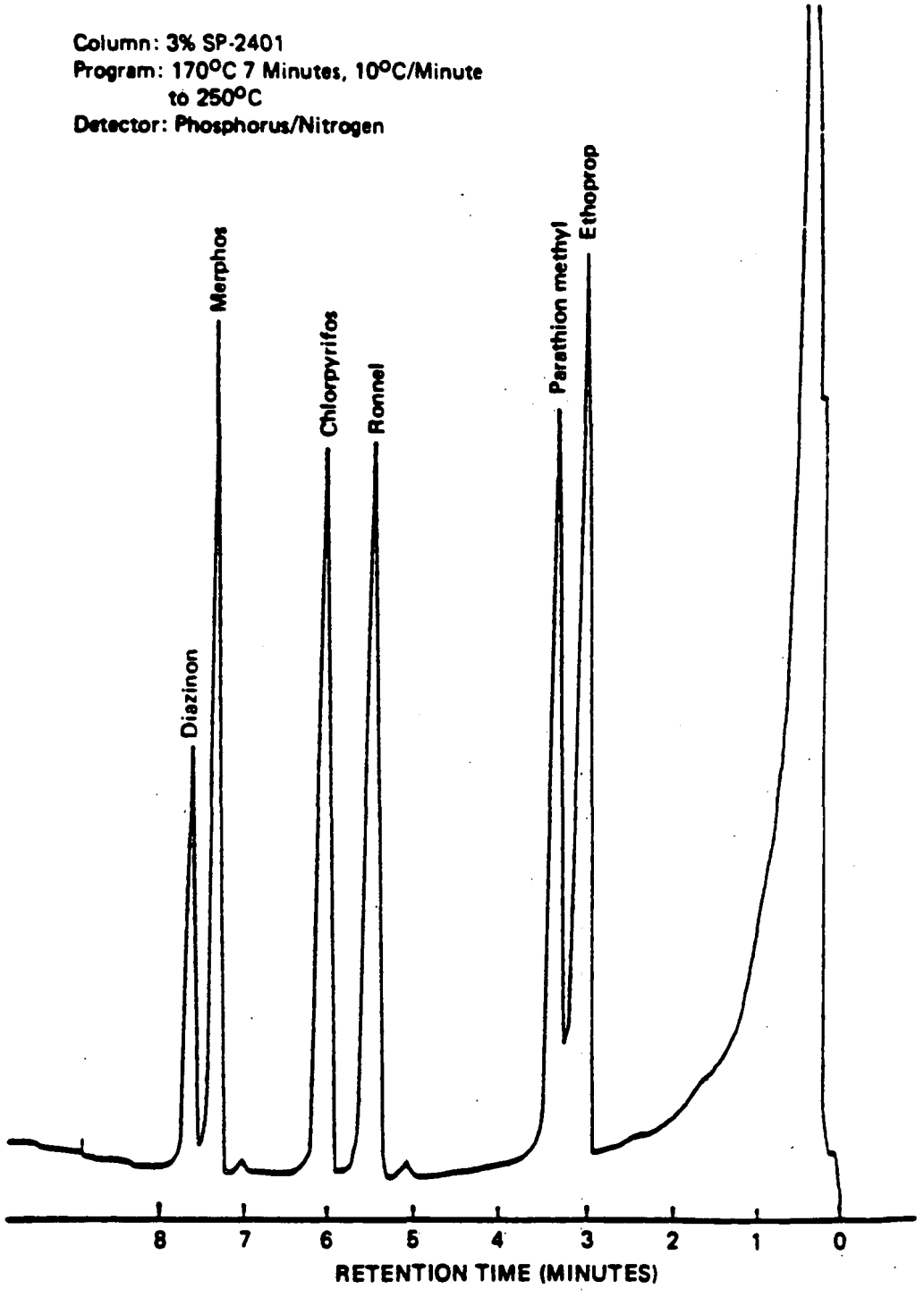


Figure 2. Gas chromatogram of organophosphorus pesticides (Example 2).

Column: 15% SE–54 on Gas Chrom Q
Temperature: 100°C Initial, then
25°C/Minute to 200°C
Detector: Hall Electrolytic Conductivity–Oxidative Mode

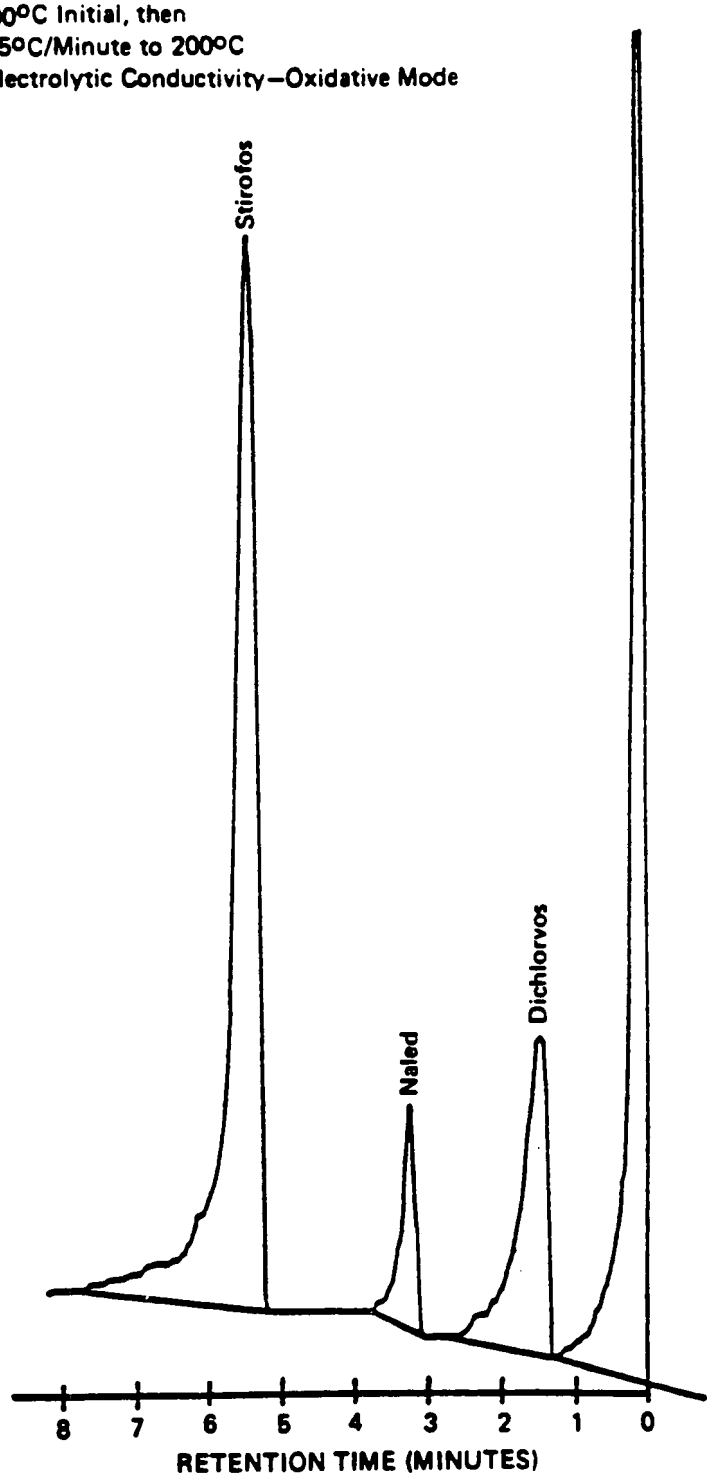


Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

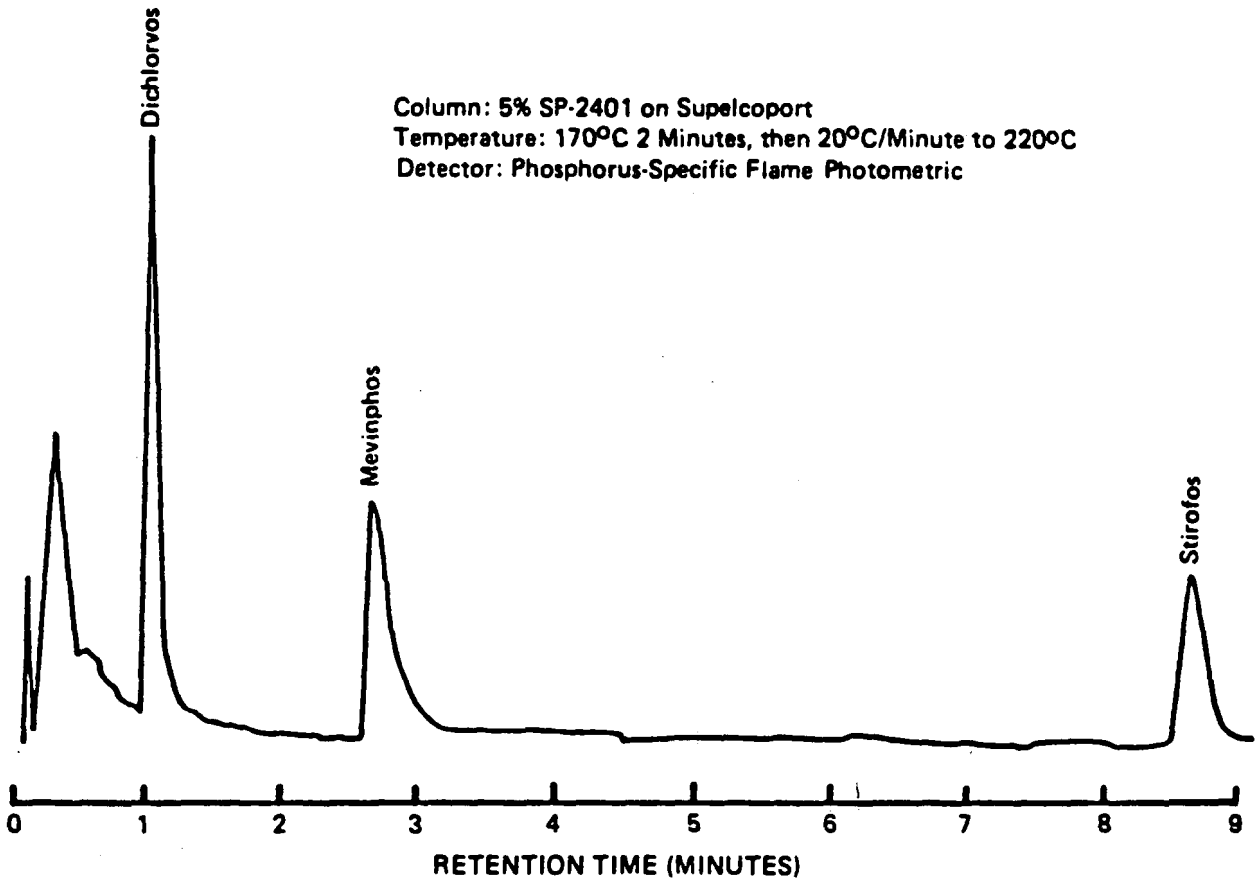


Figure 4. Gas chromatogram of organophosphorus pesticides (Example 4).

8.2.1 Select a representative spike concentration for each analyte to be measured. The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

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, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are 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:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The GC/MS operating conditions and procedures for analysis are those specified in Method 8270.

8.4.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns and additional cleanup.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 3.

10.0 REFERENCES

1. Pressley, T.A. and J.E. Longbottom, "The Determination of Organophosphorus Pesticides in Industrial and Municipal Wastewater: Method 614," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-82-004, 1982.

2. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists 48, 1037, 1965.

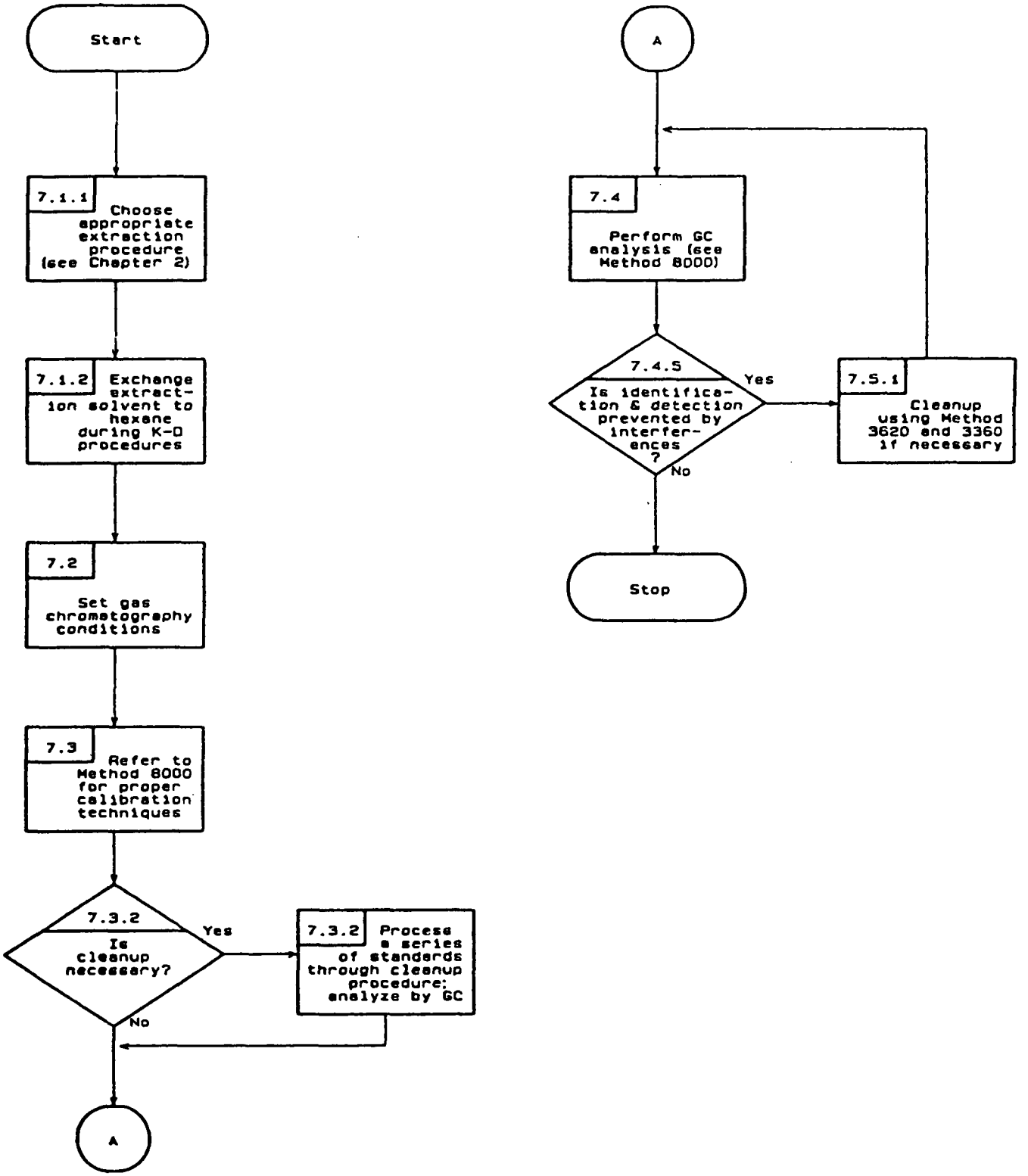
3. U.S. EPA, "Analysis of Volatile Hazardous Substances by GC/MS: Pesticide Methods Evaluation," Letter Reports 6, 12A, and 14, EPA Contract 68-03-2697, 1982.

4. U.S. EPA, "Method 622, Organophosphorous Pesticides," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268.

TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Average recovery (%)	Standard deviation (%)	Spike range (ug/L)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

[a]Information taken from Reference 4.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3620 and 3360 if necessary
No
Stop

METHOD 8150

CHLORINATED HERBICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

TABLE 1. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS FOR CHLORINATED HERBICIDES

Compound	Retention time (min)[a]				Method detection limit (ug/L)
	Col.1a	Col.1b	Col.2	Col.3	
2,4-D	2.0	-	1.6	-	1.2
2,4-DB	4.1	-	-	-	0.91
2,4,5-T	3.4	-	2.4	-	0.20
2,4,5-TP (Silvex)	2.7	-	2.0	-	0.17
Dalapon	-	-	-	5.0	5.8
Dicamba	1.2	-	1.0	-	0.27
Dichloroprop	-	4.8	-	-	0.65
Dinoseb	-	11.2	-	-	0.07
MCPA	-	4.1	-	-	249
MCPP	-	3.4	-	-	192

[a]Column conditions are given in Sections 4.1 and 7.4.

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

[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.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

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 areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 4-mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.1.2 Column 2: 1.8-m x 4-mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.1.3 Column 3: 1.98-m x 2-mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.2 **Detector:** Electron capture (ECD).

4.2 Erlenmeyer flasks: 250- and 500-mL Pyrex, with 24/40 ground-glass joint.

4.3 Beaker: 500-mL.

4.4 Diazomethane generator: Refer to Section 7.3 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 **Diazald kit:** recommended for the generation of diazomethane using the procedure given in Section 7.3.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.3.3.

4.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

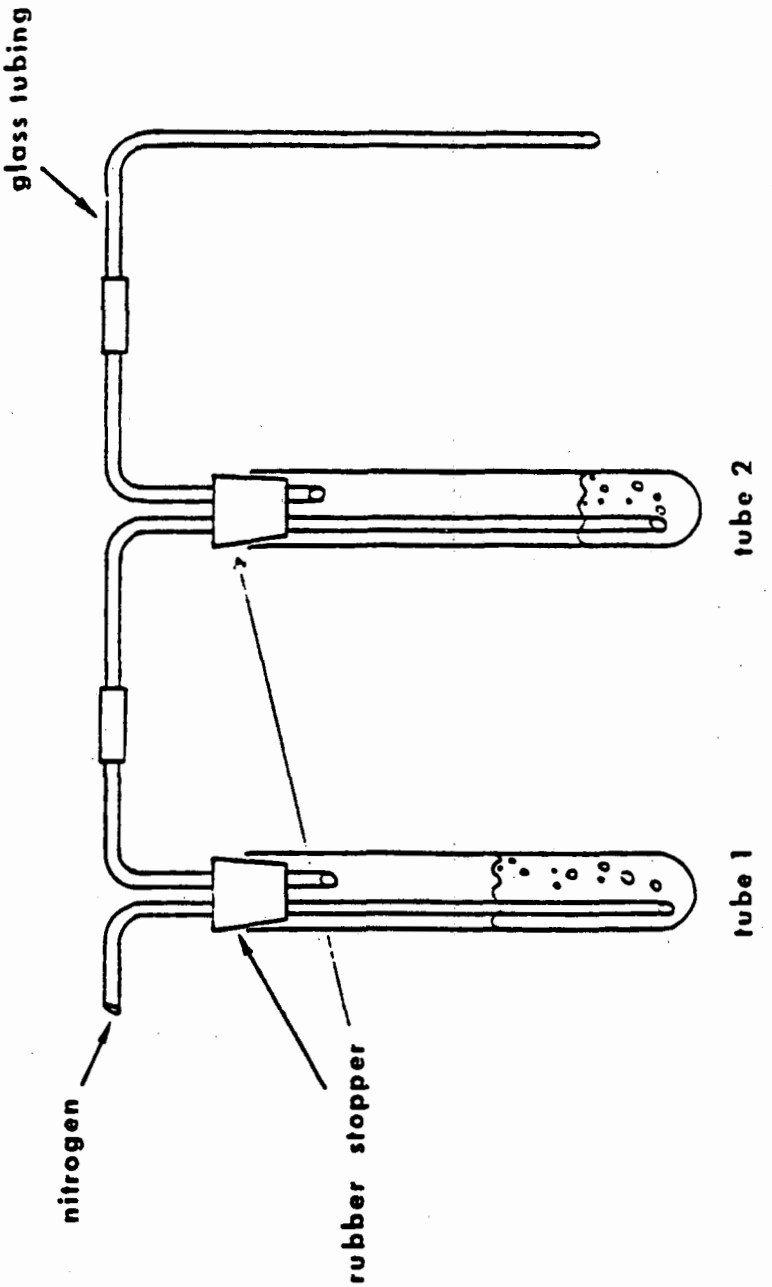


Figure 1. Diazomethane generator.

4.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

4.7 Drying column: 400-mm x 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.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). 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.

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).

4.9 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 (±5°C). The bath should be used in a hood.

4.11 Microsyringe: 10-uL.

4.12 Wrist shaker: Burrell Model 75 or equivalent.

4.13 Glass wool: Pyrex, acid washed.

4.14 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

4.15 Syringe: 5-mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

5.2 Sulfuric acid solution:

5.2.1 (1:1) (v/v) - slowly add 50 mL H_2So_4 (sp. gr. 1.84) to 50 mL of reagent water.

5.2.2 (1:3) (v/v) - slowly add 25 mL H_2So_4 (sp. gr. 1.84) to 75 mL of reagent water.

5.3 Hydrochloric acid: (ACS), (1:9) (v/v) - add one volume of concentrated HCl to 9 volumes of reagent water.

5.4 Potassium hydroxide solution: 37% aqueous solution (w/v). Dissolve 37 g ACS grade potassium hydroxide pellets in reagent water and dilute to 100 mL.

5.5 Carbitol (Diethylene glycol monoethyl ether): (ACS), available from Aldrich Chemical Co.

5.6 Solvents:

5.6.1 Acetone, methanol, ethanol, methylene chloride, hexane (pesticide quality or equivalent).

5.6.2 **Diethyl ether:** Pesticide quality or equivalent. Must be free of peroxides, as indicated by EM Quant test strips (available from Scientific Products Co., Cat. No. P1126-8, and other suppliers). Procedures recommended for removal of peroxides are provided with the test strips. After cleanup, 20 mL ethanol preservative must be added to each liter of ether.

5.7 Sodium sulfate: (ACS) granular, acidified, anhydrous. Heat treat in a shallow tray at 400°C for a minimum of 4 hr to remove phthalates and other interfering organic substances. Alternatively, heat 16 hr at 400-500°C in a shallow tray or Soxhlet extract with methylene chloride for 48 hr. Acidify by slurrying 100 g sodium sulfate with enough diethyl ether to just cover the solid; then add 0.1 mL of concentrated sulfuric acid and mix thoroughly. Remove the ether under a vacuum. Mix 1 g of the resulting solid with 5 mL of reagent water and measure the pH of the mixture. It must be below a pH of 4. Store at 130°C.

5.8 N-Methyl-N-nitroso-p-toluenesulfonamide (Diazald): (ACS) available from Aldrich Chemical Co.

5.9 Silicic acid: chromatographic grade, nominal 100 mesh. Store at 130°C.

5.10 Stock standard solutions: Stock standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.10.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure acids. Dissolve the material in pesticide quality diethyl ether and dilute to volume in a 10-mL volumetric flask. Larger

volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.10.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.11 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. 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.

5.12 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.

5.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.11.

5.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

5.12.3 Analyze each calibration standard according to Section 7.0.

5.13 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 water blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. 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, Section 4.1. Extracts must be stored under refrigeration and analyzed within 40 days of extraction.

7.0 PROCEDURE

7.1 Preparation of solid samples:

7.1.1 **Extraction:**

7.1.1.1 To a 500-mL, wide-mouth Erlenmeyer flask add 50 g (dry weight) of the well-mixed, moist solid sample. Adjust the pH to 2 with concentrated HCl and monitor the pH for 15 min with occasional stirring. If necessary, add additional HCl until the pH remains at 2.

7.1.1.2 Add 20 mL acetone to the flask and mix the contents with the wrist shaker for 20 min. Add 80 mL diethyl ether to the same flask and shake again for 20 min. Decant the extract and measure the volume of solvent recovered.

7.1.1.3 Extract the sample twice more using 20 mL of acetone followed by 80 mL of diethyl ether. After addition of each solvent, the mixture should be shaken with the wrist shaker for 10 min and the acetone-ether extract decanted.

7.1.1.4 After the third extraction, the volume of extract recovered should be at least 75% of the volume of added solvent. If this is not the case, additional extractions may be necessary. Combine the extracts in a 2-liter separatory funnel containing 250 mL of 5% acidified sodium sulfate. If an emulsion forms, slowly add 5 g of acidified sodium sulfate (anhydrous) until the solvent-water mixture separates. A quantity of acidified sodium sulfate equal to the weight of the sample may be added, if necessary.

7.1.1.5 Check the pH of the extract. If it is not at or below pH 2, add more concentrated HCl until stabilized at the desired pH. Gently mix the contents of the separatory funnel for 1 min and allow the layers to separate. Collect the aqueous phase in a clean beaker and the extract phase (top layer) in a 500-mL ground-glass Erlenmeyer flask. Place the aqueous phase back into the separatory funnel and re-extract using 25 mL of diethyl ether. Allow the layers to separate and discard the aqueous layer. Combine the ether extracts in the 500-mL Erlenmeyer flask.

7.1.2 **Hydrolysis:**

7.1.2.1 Add 30 mL of reagent water, 5 mL of 37% KOH, and one or two clean boiling chips to the flask. Place a three-ball Snyder column on the flask, evaporate the diethyl ether on a water bath, and continue to heat for a total of 90 min.

7.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.3 **Solvent cleanup:**

7.1.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.1.3.2 Combine ether extracts in a 125-mL Erlenmeyer flask containing 1.0 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

7.1.3.3 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.1.3.4 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 diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the

bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether. Proceed to Section 7.3 for esterification.

7.2 Preparation of liquid samples:

7.2.1 Extraction:

7.2.1.1 Mark the water miniscus on the side of the sample container for later determination of sample volume. Pour the entire sample into a 2-liter separatory funnel and check the pH with wide-range pH paper. Adjust the pH to less than 2 with sulfuric acid (1:1).

7.2.1.2 Add 150 mL of diethyl ether to the sample bottle, seal, and shake for 30 sec to rinse the walls. Transfer the solvent wash to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water layer for a minimum of 10 min. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Drain the aqueous phase into a 1-liter Erlenmeyer flask. Collect the solvent extract in a 250-mL ground-glass Erlenmeyer flask containing 2 mL of 37% KOH. Approximately 80 mL of the diethyl ether will remain dissolved in the aqueous phase.

7.2.1.3 Repeat the extraction two more times using 50 mL of diethyl ether each time. Combine the extracts in the Erlenmeyer flask. (Rinse the 1-liter flask with each additional aliquot of extracting solvent.)

7.2.2 Hydrolysis:

7.2.2.1 Add one or two clean boiling chips and 15 mL of reagent water to the 250-mL flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top of the column. Place the apparatus on a hot water bath (60°-65°C) so that the bottom of the flask is bathed with hot water vapor. Although the diethyl ether will evaporate in about 15 min, continue heating for a total of 60 min, beginning from the time the flask is placed in the water bath. Remove the apparatus and let stand at room temperature for at least 10 min.

7.2.2.2 Transfer the solution to a 60-mL separatory funnel using 5-10 mL of reagent water. Wash the basic solution twice by shaking for 1 min with 20-mL portions of diethyl ether. Discard the organic phase. The herbicides remain in the aqueous phase.

7.2.3 **Solvent cleanup:**

7.2.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.2.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.3 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 diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.2.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.2.3.5 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

7.3 Esterification:

7.3.1 Two methods may be used for the generation of diazomethane: the bubbler method (set up shown in Figure 1) and the Diazald kit method. The bubbler method is suggested when small batches (10-15) of samples require esterification. The bubbler method works well with samples that have low concentrations of herbicides (e.g., aqueous samples) and is safer to use than the Diazald kit procedure. The Diazald kit method is good for large quantities of samples needing esterification. The Diazald kit method is more effective than the bubbler method for soils or samples that may contain high concentrations of herbicides (e.g., samples such as soils that may result in yellow extracts following hydrolysis may be difficult to handle by the bubbler method). The diazomethane derivatization (U.S. EPA, 1971) procedures, described below, will react efficiently with all of the chlorinated herbicides described in this method and should be used only by experienced analysts, due to the potential hazards associated with its use. The following precautions should be taken:

CAUTION: Diazomethane is a carcinogen and can explode under certain conditions.

- Use a safety screen.
- Use mechanical pipetting aides.
- Do not heat above 90°C -- EXPLOSION may result.
- Avoid grinding surfaces, ground-glass joints, sleeve bearings, glass stirrers -- EXPLOSION may result.
- Store away from alkali metals -- EXPLOSION may result.
- Solutions of diazomethane decompose rapidly in the presence of solid materials such as copper powder, calcium chloride, and boiling chips.

7.3.2 **Diazald kit method:** Instructions for preparing diazomethane are provided with the generator kit.

7.3.2.1 Add 2 mL of diazomethane solution and let sample stand for 10 min with occasional swirling.

7.3.2.2 Rinse inside wall of ampule with several hundred uL of diethyl ether. Allow solvent to evaporate spontaneously at room temperature to about 2 mL.

7.3.2.3 Dissolve the residue in 5 mL of hexane. Analyze by gas chromatography.

7.3.3 **Bubbler method:** Assemble the diazomethane bubbler (see Figure 1).

7.3.3.1 Add 5 mL of diethyl ether to the first test tube. Add 1 mL of diethyl ether, 1 mL of carbitol, 1.5 mL of 37% KOH, and 0.1-0.2 g Diazald to the second test tube. Immediately place the exit tube into the concentrator tube containing the sample extract.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total esterification.

7.3.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 min.

7.3.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.4 Gas chromatography conditions (Recommended):

7.4.1 **Column 1a:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.2 **Column 1b:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 140°C for 6 min and then programmed at 10°C/min to 200°C and held.

7.4.3 **Column 2:** Set 5% methane/95% argon carrier gas at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.4 **Column 3:** Set nitrogen (ultra-high purity) carrier gas at 25-mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 10°C/min to 150°C and held.

7.5 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.

7.5.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.5.2 The following gas chromatographic columns are recommended for the compounds indicated:

Parameter	Column
Dicamba	1a,2
2,4-D	1a,2
2,4,5-TP	1a,2
2,4,5-T	1a,2
2,4-DB	1a
Dalapon	3
MCPP	1b
MCPA	1b
Dichloroprop	1b
Dinoseb	1b

7.6 Gas chromatographic analysis:

7.6.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.6.2 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-level standard after each group of 10 samples in the analysis sequence.

7.6.3 Examples of chromatograms for various chlorophenoxy herbicides are shown in Figures 2 through 4.

7.6.4 Record the sample volume injected and the resulting peak sizes (in area units or peak heights).

7.6.5 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.

7.6.6 If calibration standards have been analyzed in the same manner as the samples (e.g., have undergone hydrolysis and esterification), then the calculation of concentration given in Method 8000, Section 7.8 should be used. However, if calibration is done using standards made from methyl ester compounds (compounds not esterified by application of this method), then the calculation of concentration must include a correction for the molecular weight of the methyl ester versus the acid herbicide.

7.6.7 If peak detection and identification are prevented due to interferences, further cleanup is required. Before using any cleanup procedure, the analyst must process a series of standards through the procedure to validate elution patterns and the absence of interferences from reagents.

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

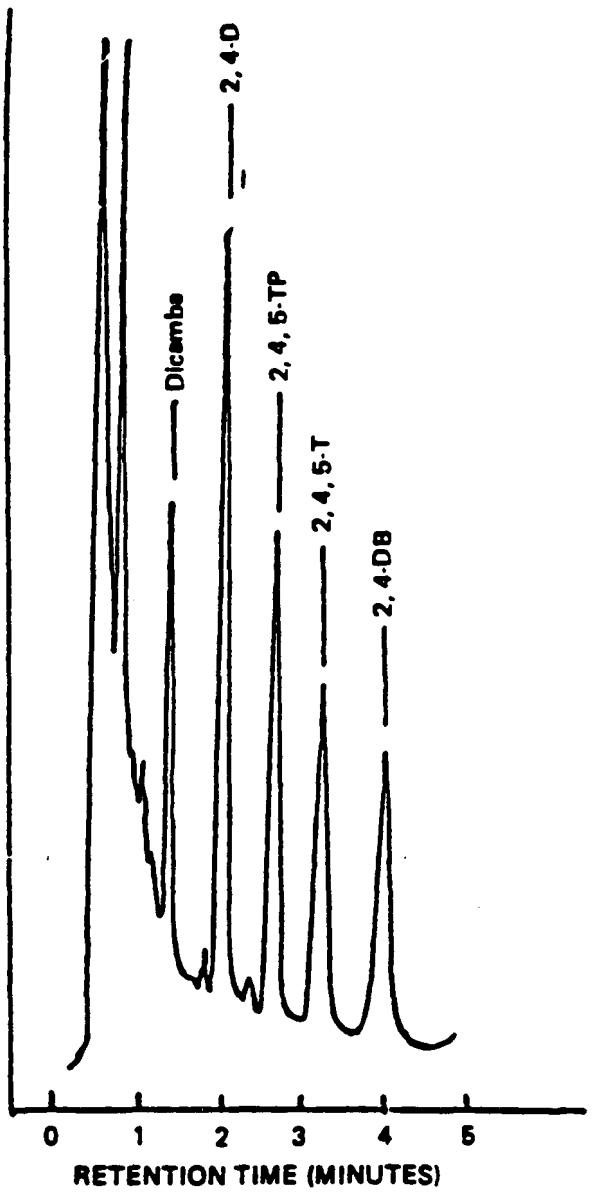


Figure 2. Gas chomatogram of chlorinated herbicides.

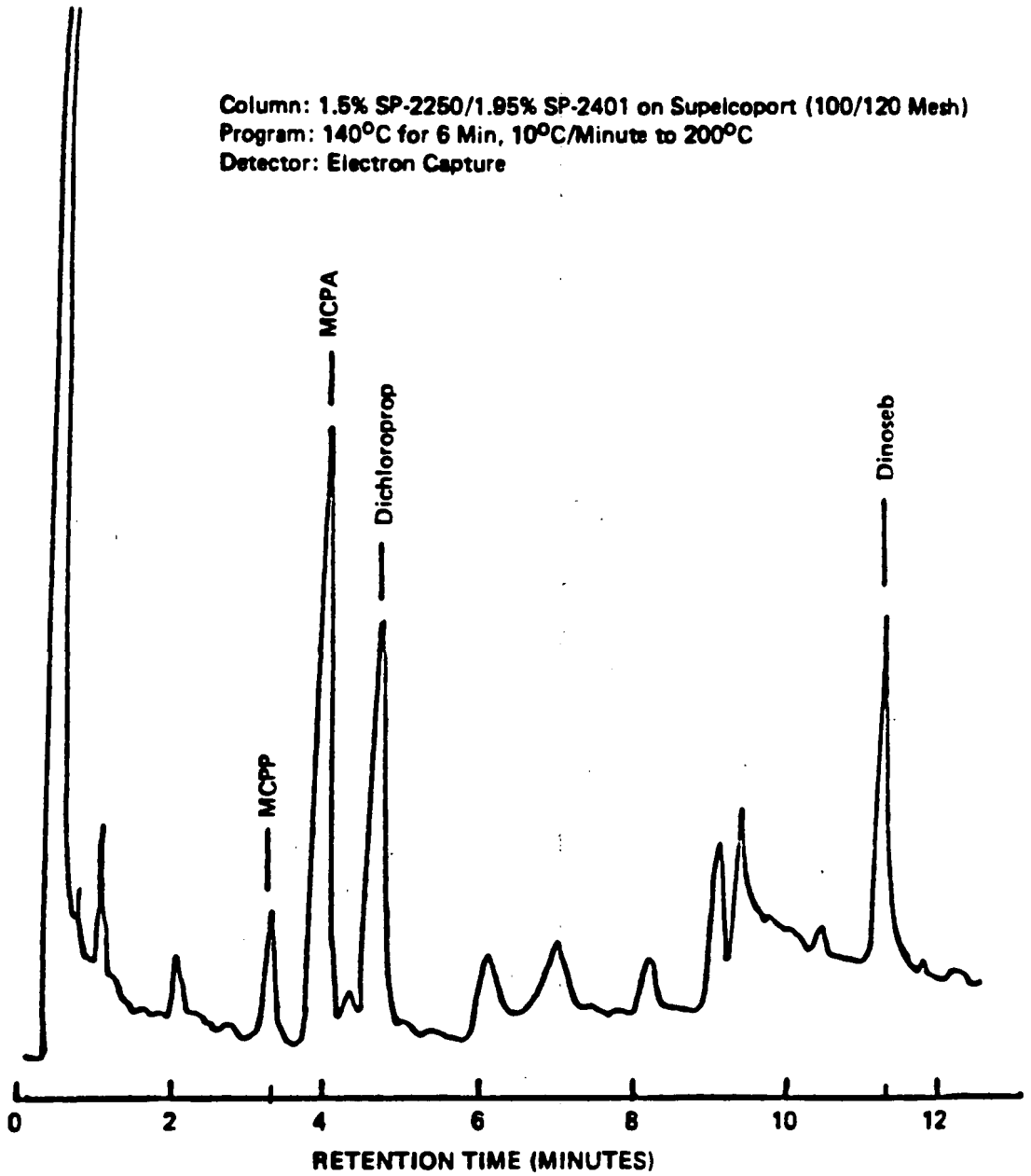


Figure 3. Gas chromatogram of chlorinated herbicides.

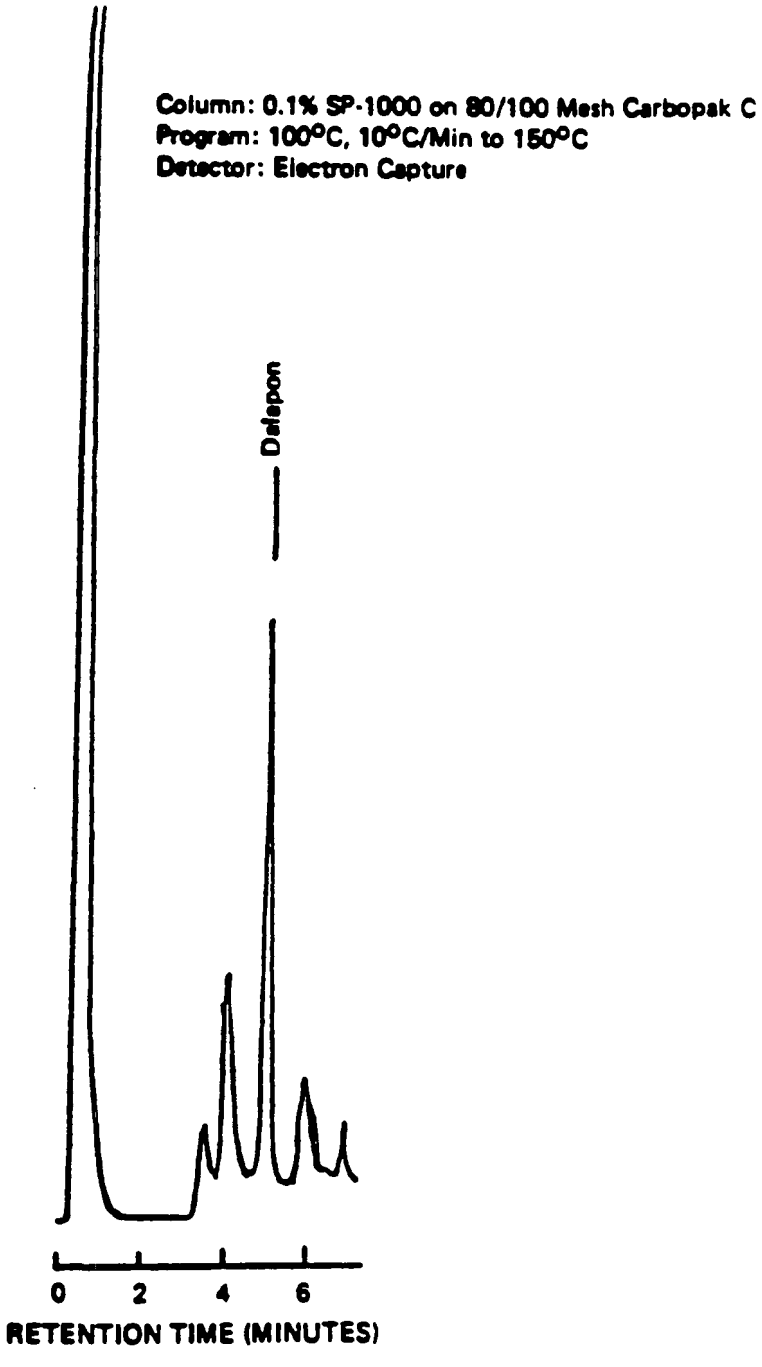


Figure 4. Gas chromatogram of dalapon, column 3.

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, Section 8.6.

8.2.1 Select a representative spike concentration for each compound (acid or ester) to be measured. Using stock standards, prepare a quality control check sample concentrate in acetone 1,000 times more concentrated than the selected concentrations.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

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, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are 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:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. Refer to Method 8270 for the appropriate GC/MS operating conditions and analysis procedures.

8.4.2 When available, chemical ionization mass spectra may be employed to aid the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns or additional cleanup.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

1. U.S. EPA, National Pollutant Discharge Elimination System, Appendix A, Fed. Reg., 38, No. 75, Pt. II, Method for Chlorinated Phenoxy Acid Herbicides in Industrial Effluents, Cincinnati, Ohio, 1971.

2. Goerlitz, D.G., and W.L. Lamar, "Determination of Phenoxy Acid Herbicides in Water by Electron Capture and Microcoulometric Gas Chromatography," U.S. Geol. Survey Water Supply Paper, 1817-C, 1967.

3. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

4. U.S. EPA, "Extraction and Cleanup Procedure for the Determination of Phenoxy Acid Herbicides in Sediment," EPA Toxicant and Analysis Center, Bay St. Louis, Mississippi, 1972.

5. "Pesticide Methods Evaluation," Letter Report #33 for EPA Contract No. 68-03-2697. Available from U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268.

6. McNair, H.M. and E.J. Bonelli, "Basic Chromatography," Consolidated Printing, Berkeley, California, p. 52, 1969.

7. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.

8. Glaser, J.A. et.al., "Trace Analysis for Wastewaters," Environmental Science & Technology, 15, 1426, 1981.

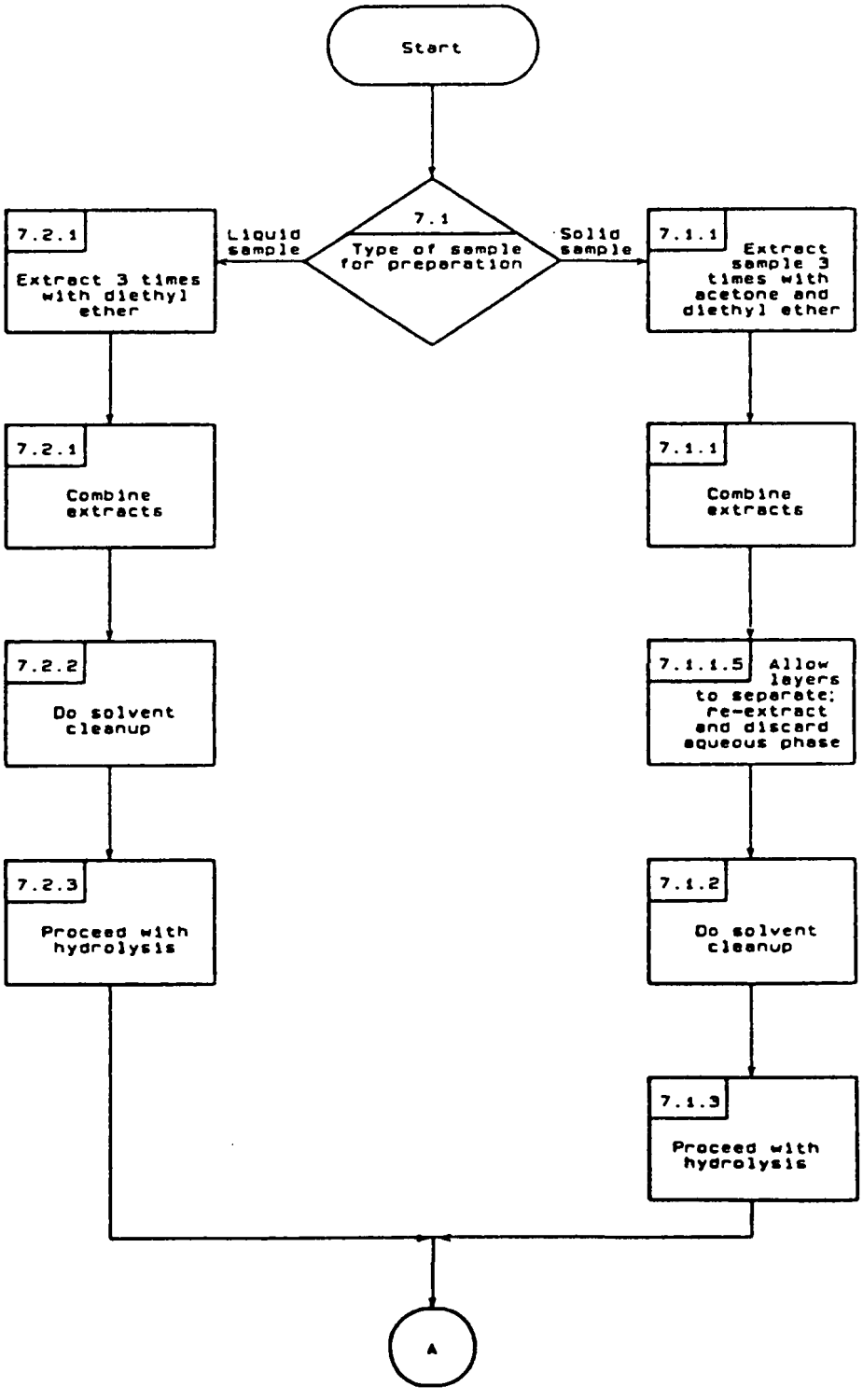
9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.

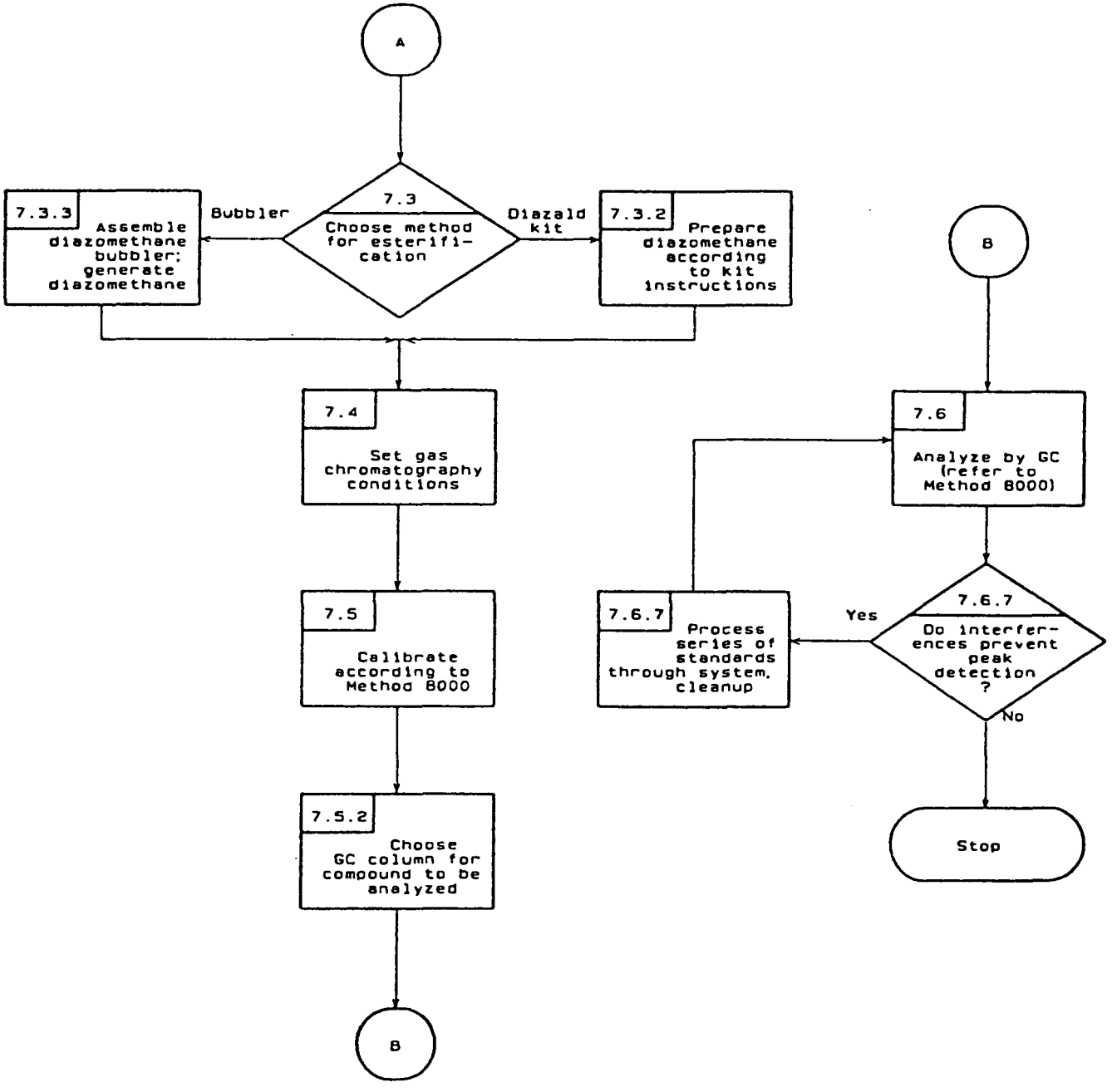
TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Sample Type	Spike (ug/L)	Mean Recovery (%)	Standard deviation (%)
2,4-D	DW	10.9	75	4
	MW	10.1	77	4
	MW	200	65	5
Dalapon	DW	23.4	66	8
	MW	23.4	96	13
	MW	468	81	9
2,4-DB	DW	10.3	93	3
	MW	10.4	93	3
	MW	208	77	6
Dicamba	DW	1.2	79	7
	MW	1.1	86	9
	MW	22.2	82	6
Dichlorprop	DW	10.7	97	2
	MW	10.7	72	3
	MW	213	100	2
Dinoseb	MW	0.5	86	4
	MW	102	81	3
MCPA	DW	2020	98	4
	MW	2020	73	3
	MW	21400	97	2
MCPP	DW	2080	94	4
	MW	2100	97	3
	MW	20440	95	2
2,4,5-T	DW	1.1	85	6
	MW	1.3	83	4
	MW	25.5	78	5
2,4,5-TP	DW	1.0	88	5
	MW	1.3	88	4
	MW	25.0	72	5

[a]All results based upon seven replicate analyses. Esterification performed using the bubbler method. Data obtained from reference 9.

DW = Reagent water
MW = Municipal water


Start
7.1
Type of sample for preparation
Liquid sample
Solid sample
7.2.1
Extract 3 times with diethyl ether
7.1.1
Extract sample 3 times with acetone and diethyl ether
7.2.1
Combine extracts
7.1.1
Combine extracts
7.2.2
Do solvent cleanup
7.1.1.5
Allow layers to separate; re-extract and discard aqueous phase
7.2.3
Proceed with hydrolysis
7.1.2
Do solvent cleanup
7.1.3
Proceed with hydrolysis
A


A
7.3
Choose method for esterification
Bubbler
Diazald kit
7.3.3
Assemble diazomethane bubbler; generate diazomethane
7.3.2
Prepare diazomethane according to kit instructions
7.4
Set gas chromatography conditions
7.5
Calibrate according to Method 8000
7.5.2
Choose GC column for compound to be analyzed
B
B
7.6
Analyze by GC (refer to Method 8000)
7.6.7
Do interferences prevent peak detection ?
Yes
No
7.6.7
Process series of standards through system, cleanup
Stop

METHOD 8240

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 Method 8240 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including 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.

1.2 Method 8240 can be used to quantify most volatile organic compounds that have boiling points below 200°C [vapor pressure is approximately equal to mm Hg @ 25°C] and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique, however, for the more soluble compounds, quantitation limits 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. See Table 1 for a list of compounds, retention times, and their characteristic ions that have been evaluated on a purge-and-trap GC/MS system.

1.3 The practical quantitation limit (PQL) of Method 8240 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 2). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8240 is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.5 To increase purging efficiencies of acrylonitrile and acrolein, refer to Methods 5030 and 8030 for proper purge-and-trap conditions.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). The components are separated via the gas chromatograph and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The chromatographic conditions, as well as typical mass spectrometer operating parameters, are given.

TABLE 1. RETENTION TIMES AND CHARACTERISTIC IONS FOR VOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acetone	--	43	58
Acrolein	--	56	55, 58
Acrylonitrile	--	53	52, 51
Benzene	17.0	78	52, 77
Bromochloromethane (I.S.)	9.3	128	49, 130, 51
Bromodichloromethane	14.3	83	85, 129
4-Bromofluorobenzene (surr.)	28.3	95	174, 176
Bromoform	19.8	173	171, 175, 252
Bromomethane	3.1	94	96, 79
2-Butanone	--	72	57, 43
Carbon disulfide	--	76	78
Carbon tetrachloride	13.7	117	119, 121
Chlorobenzene	24.6	112	114, 77
Chlorobenzene-d_5 (I.S.)	--	117	82, 119
Chlorodibromomethane	--	129	208, 206
Chloroethane	4.6	64	66, 49
2-Chloroethyl vinyl ether	18.6	63	65, 106
Chloroform	11.4	83	85, 47
Chloromethane	2.3	50	52, 49
Dibromomethane	--	93	174, 95
1,4-Dichloro-2-butane	--	75	53, 89
Dichlorodifluoromethane	--	85	87, 50, 101
1,1-Dichloroethane	--	63	65, 83
1,2-Dichloroethane	10.1	62	64, 98
1,2-Dichloroethane-d_4 (surr.)	12.1	65	102
1,1-Dichloroethene	9.0	96	61, 98
trans-1,2-Dichloroethene	10.0	96	61, 98
1,2-Dichloropropane	15.7	63	62, 41
cis-1,3-Dichloropropene	15.9	75	77, 39
trans-1,3-Dichloropropene	17.2	75	77, 39
1,4-Difluorobenzene (I.S.)	19.6	114	63, 88
Ethanol	--	31	45, 27, 46
Ethylbenzene	26.4	106	91
Ethyl methacrylate	--	69	41, 39, 99
2-Hexanone	--	43	58, 57, 100
Iodomethane	--	142	127, 141
Methylene chloride	6.4	84	49, 51, 86
4-Methyl-2-pentanone	--	43	58, 100
Styrene	--	104	78, 103
1,1,2,2-Tetrachloroethane	22.1	83	85, 131, 133
Tetrachloroethene	22.2	164	129, 131, 166
Toluene	23.5	92	91, 65
Toluene-d_8 (surr.)	--	98	70, 100

TABLE 1. - Continued

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
1,1,1-Trichloroethane	13.4	97	99, 117
1,1,2-Trichloroethane	17.2	97	83, 85, 99
Trichloroethene	16.5	130	95, 97, 132
Trichlorofluoromethane	8.3	101	103, 66
1,2,3-Trichloropropane	--	75	110, 77, 61
Vinyl acetate	--	43	86
Vinyl chloride	3.8	62	64, 61
Xylene	--	106	91

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR VOLATILE ORGANICS[a]

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
1. Chloromethane	74-87-3	10	10
2. Bromomethane	74-83-9	10	10
3. Vinyl Chloride	75-01-4	10	10
4. Chloroethane	75-00-3	10	10
5. Methylene Chloride	75-09-2	5	5
6. Acetone	67-64-1	100	100
7. Carbon Disulfide	75-15-0	5	5
8. 1,1-Dichloroethene	75-35-4	5	5
9. 1,1-Dichloroethane	75-35-3	5	5
10. trans-1,2-Dichloroethene	156-60-5	5	5
11. Chloroform	67-66-3	5	5
12. 1,2-Dichloroethane	107-06-2	5	5
13. 2-Butanone	78-93-3	100	100
14. 1,1,1-Trichloroethane	71-55-6	5	5
15. Carbon Tetrachloride	56-23-5	5	5
16. Vinyl Acetate	108-05-4	50	50
17. Bromodichloromethane	75-27-4	5	5
18. 1,1,2,2-Tetrachloroethane	79-34-5	5	5
19. 1,2-Dichloropropane	78-87-5	5	5
20. trans-1,3-Dichloropropene	10061-02-6	5	5
21. Trichloroethene	79-01-6	5	5
22. Dibromochloromethane	124-48-1	5	5
23. 1,1,2-Trichloroethane	79-00-5	5	5
24. Benzene	71-43-2	5	5
25. cis-1,3-Dichloropropene	10061-01-5	5	5
26. 2-Chloroethyl Vinyl Ether	110-75-8	10	10
27. Bromoform	75-25-2	5	5
28. 2-Hexanone	591-78-6	50	50
29. 4-Methyl-2-pentanone	108-10-1	50	50
30. Tetrachloroethene	127-18-4	5	5

TABLE 2. - Continued

Volatiles	CAS Number	Practical Quantitation Limits[b] Ground water ug/L	Low Soil/Sediment ug/Kg
31. Toluene	108-88-3	5	5
32. Chlorobenzene	108-90-7	5	5
33. Ethyl Benzene	100-41-4	5	5
34. Styrene	100-42-5	5	5
35. Total Xylenes		5	5

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the % moisture in each sample.

Other Matrices:	Factor[1]
Water miscible liquid waste	50
High-level soil & sludges	125
Non-water miscible waste	500

[1]PQL = [PQL for ground water (Table 2)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

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/MS following the normal water method.

2.3 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 trapped. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column. The gas chromatographic column is heated to elute the components, which are detected with a mass spectrometer.

3.0 INTERFERENCES

3.1 Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. The analytical system, however, should be checked to ensure freedom from interferences, under the analysis conditions, by analyzing method blanks.

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

3.3 Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of reagent water to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents.

3.5 Impurities in the purge gas and from organic compounds out-gasing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running 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.

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 screw caps and Teflon liners or glass culture tubes with a screw cap and Teflon liner.

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 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.11 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.

4.11.1 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 utilized, provided equivalent performance is demonstrated.

4.11.2 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 Figure 2). 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

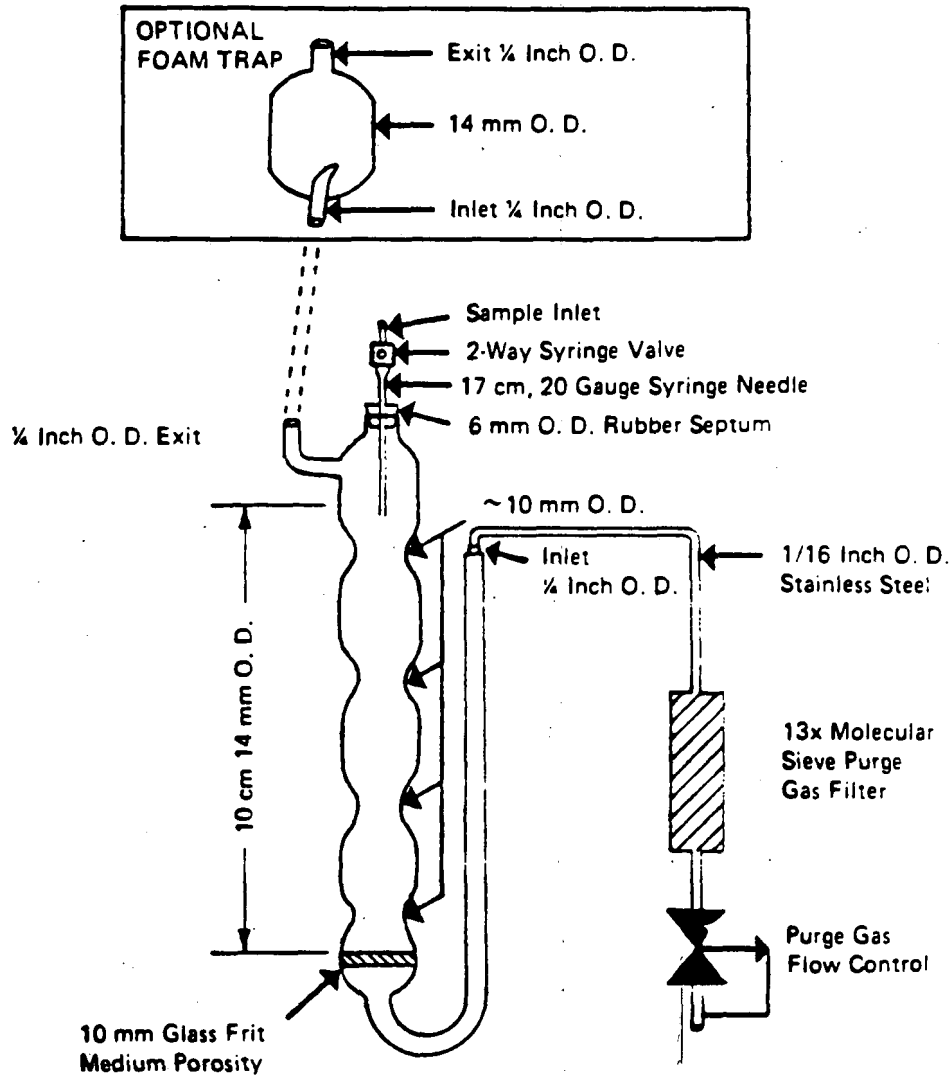


Figure 1. Purging chamber.

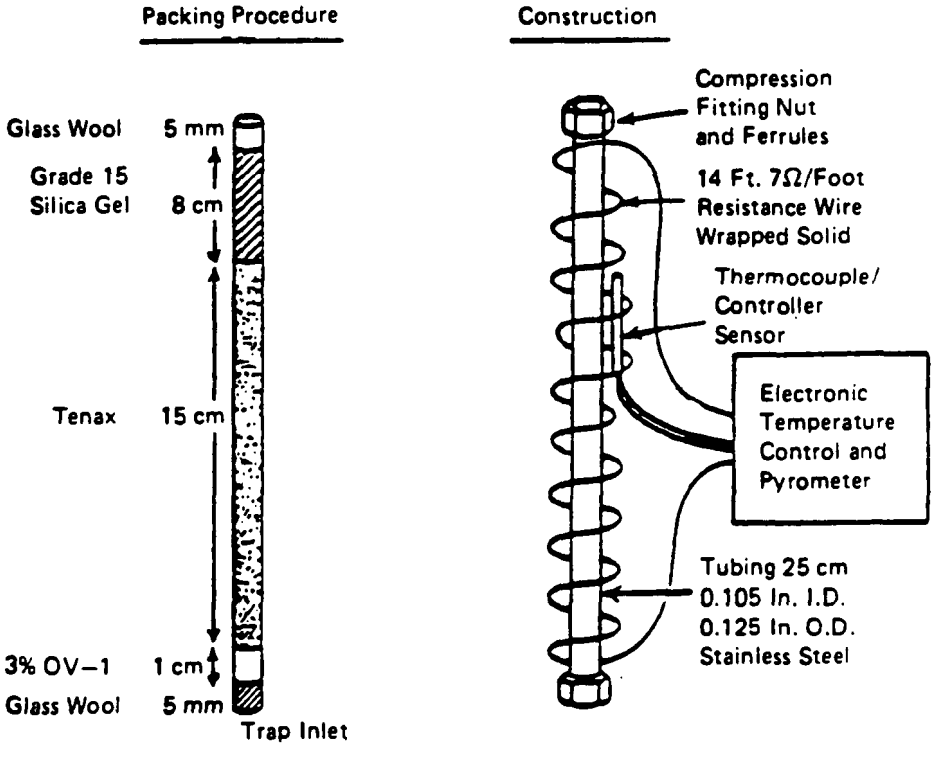


Figure 2. Trap packings and construction to include desorb capability for Method 8240.

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 room, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min 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.

4.11.3 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 Figure 2 meets these criteria.

4.11.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.11.5 **Trap Packing Materials:**

4.11.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

4.11.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

4.11.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through 26 mesh screen.

4.12 Gas chromatograph/mass spectrometer system:

4.12.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.12.2 **Column:** 6-ft x 0.1-in. I.D. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh) or equivalent.

4.12.3 **Mass spectrometer:** Capable of scanning from 35-260 amu every 3 sec or less, using 70 volts (nominal) electron energy in the electron impact mode and producing a mass spectrum that meets all the criteria in Table 3 when 50 ng of 4-bromofluorobenzene (BFB) are injected through the gas chromatograph inlet.

4.12.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 3) may be used. GC-to-MS interfaces constructed entirely of glass or of

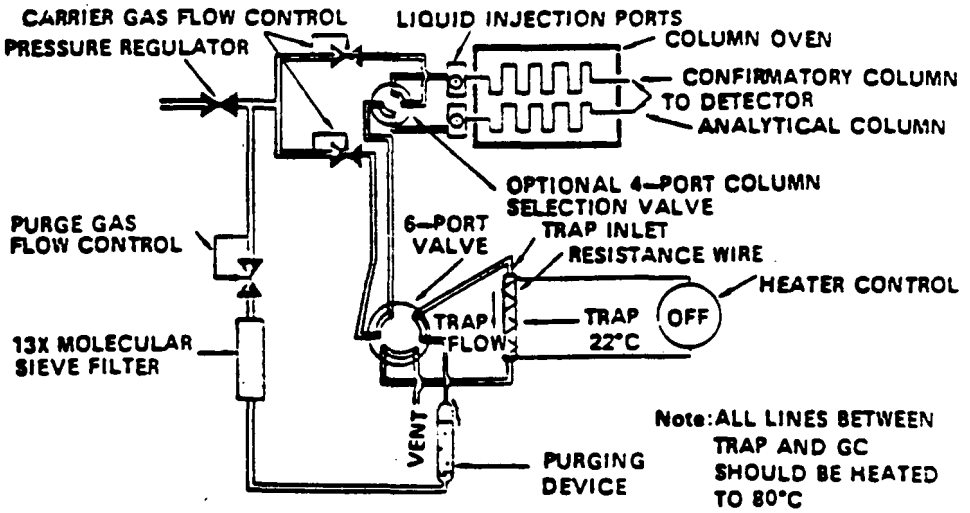


Figure 3. Schematic of purge-and-trap device – purge mode for Method 8240.

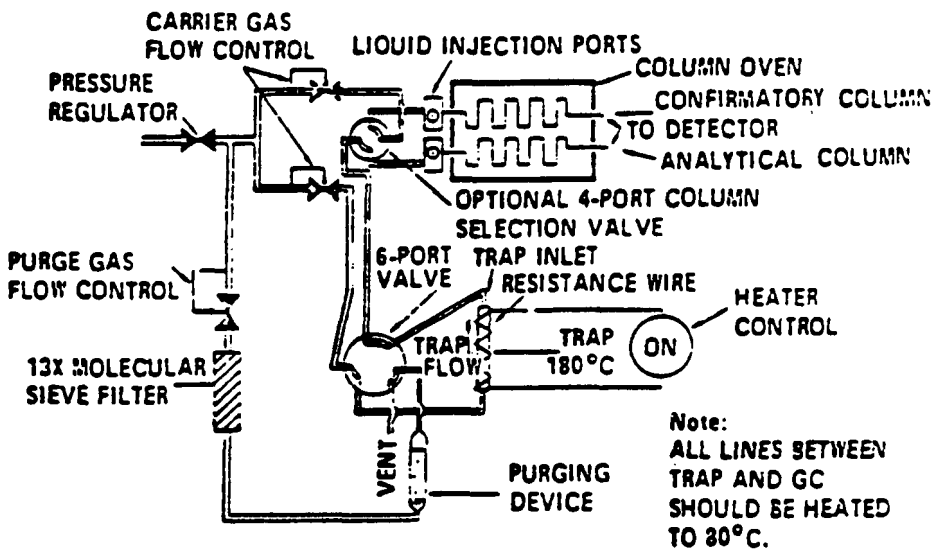


Figure 4. Schematic of purge-and-trap device – desorb mode for Method 8240.

TABLE 3. BFB KEY ION ABUNDANCE CRITERIA

Mass	Ion Abundance Criteria
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane.

4.12.5 **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 GC/MS 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 integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

5.0 REAGENTS

5.1 Stock solutions: Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.1.1 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 0.1 mg.

5.1.2 Add the assayed reference material, as described below.

5.1.2.1 Liquids: Using a 100-uL 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.

5.1.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared 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.

5.1.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) 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.

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

5.1.5 Prepare fresh standards every two months for gases. Reactive compounds such as 2-chloroethylvinyl ether and 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.

5.2 Secondary dilution standards: Using stock standard solutions, prepare in 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.

5.3 Surrogate standards: The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and 1,2-dichloroethane-d_4. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Section 5.1, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.4 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 detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Sections 5.1 and 5.2. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.5 4-Bromofluorobenzene (BFB) standard: A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.6 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Sections 5.1 and 5.2). Prepare these solutions in reagent water. 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 not exceed the working range of the GC/MS system. 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). Store for one week only in a vial with no headspace.

5.7 Matrix spiking standards: Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The suggested compounds are 1,1-dichloroethene,

trichloroethene, chlorobenzene, toluene, and benzene. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.8 Great care must be taken to maintain the integrity of all standard solutions. It is recommended that all standards be stored at -10°C to -20°C in screw-cap amber bottles with Teflon liners.

5.9 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit (MDL) of the parameters of interest.

5.9.1 Reagent 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).

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

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

5.10 Methanol: Pesticide quality or equivalent. Store apart from other solvents.

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 Direct injection: In very limited applications (e.g., aqueous process wastes), direct injection of the sample into the GC/MS 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).

7.2 Initial calibration for purge-and-trap procedure:

7.2.1 **Recommended GC/MS operating conditions:**

Electron energy:	70 volts (nominal).
Mass range:	35-260 amu.
Scan time:	To give 5 scans/peak but not to exceed 7 sec/scan.
Initial column temperature:	45°C.
Initial column holding time:	3 min.
Column temperature program:	8°C/min.
Final column temperature:	220°C.
Final column holding time:	15 min.
Injector temperature:	200-225°C.
Source temperature:	According to manufacturer's specifications.
Transfer line temperature:	250-300°C.
Carrier gas:	Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.2.2 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection or purging of 4-bromofluorobenzene (2-uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.3 Assemble a purge-and-trap device that meets the specification in Section 4.11. 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 min while backflushing at 180°C with the column at 220°C.

7.2.4 Connect the purge-and-trap device to a gas chromatograph.

7.2.5 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of reagent water to the purging device. The reagent 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-uL or 25-uL micro-syringe equipped with a long needle (Paragraph 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards (Paragraph 5.6). 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 uL of the internal standard solution (Paragraph 5.4). Close the 2-way syringe valve at the sample inlet.

7.2.6 Carry out the purge-and-trap analysis procedure as described in Section 7.4.1.

7.2.7 Tabulate the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Section 7.5.2). 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.

7.2.8 The average RF must be calculated for each compound. A system performance check should be made before this 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:

7.2.8.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.8.2 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. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio may improve bromoform response.

7.2.8.3 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.

7.2.9 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs).

$$\%RSD = \frac{SD}{\bar{x}} \times 100$$

where:

RSD = relative standard deviation.

$\bar{x}$ = mean of 5 initial RFs for a compound.

SD = standard deviation of average RFs for a compound.

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

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.

7.3 Daily GC/MS calibration:

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 3 before sample analysis begins. These criteria must be demonstrated each 12-hr shift.

7.3.2 The initial calibration curve (Section 7.2) for each compound of interest must be checked and verified once every 12 hr of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Paragraph 7.3.3) and CCC (Paragraph 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs): A system performance check must be made each 12 hr. 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 met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Paragraph 7.2.9 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_c = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (>25% difference), for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins.

7.3.5 The 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 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis:

7.4.1 **Water samples:**

7.4.1.1 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 used are: the headspace sampler (Method 3810) using 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 and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Paragraph 7.2.1.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Section 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min 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 (see Section 7.2.8).

7.4.1.6 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 hr. Care must be taken to prevent air from leaking into the syringe.

7.4.1.7 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.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10-to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this quantity of reagent water to the flask.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Paragraph 7.4.1.6 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 above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as i n Paragraph 7.4.1.6.

7.4.1.8 Add 10.0 uL of surrogate spiking solution (Paragraph 5.3) and 10 uL of internal standard spiking solution (Paragraph 5.4) 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. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.9 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.

7.4.1.10 Close both valves and purge the sample for 11.0 $\pm$ 0.1 min at ambient temperature.

7.4.1.11 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/MS 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 4 min. If this rapid heating requirement cannot be met, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the recommended initial program temperature of 45°C.

7.4.1.12 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 reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

7.4.1.13 After desorbing the sample for 4 min, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; 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. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7 min, 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.

7.4.1.14 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. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions from a compound, this analysis must be followed by a blank reagent 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.

7.4.1.15 For matrix spike analysis, add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.16 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 Sections 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 **Water-miscible liquids:**

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with reagent water.

7.4.2.2 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 reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with reagent water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 **Sediment/soil and waste samples:** It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. 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).

7.4.3.1 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 reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples. See Figure 5 for an illustration of a low soils impinger.

7.4.3.1.1 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.

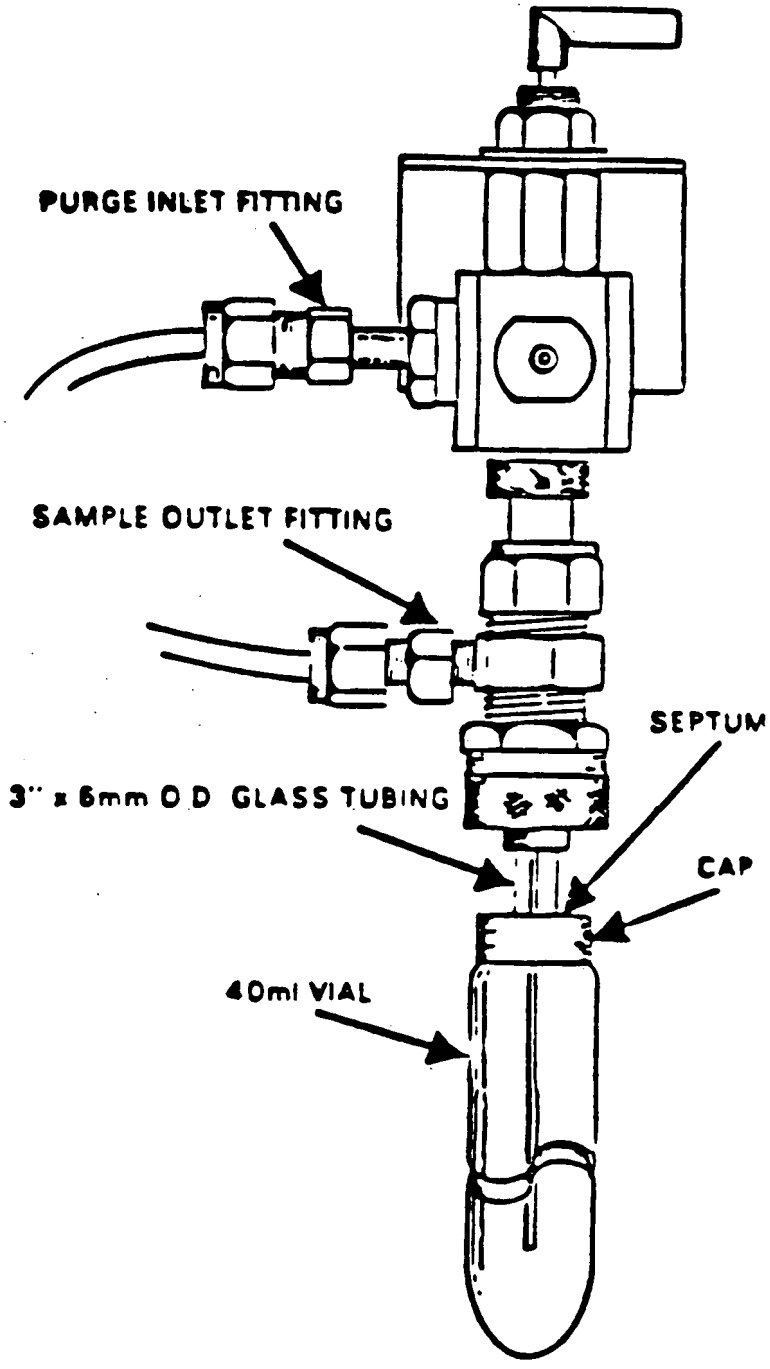


Figure 5. Low Soils Impinger

7.4.3.1.2 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. 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.

7.4.3.1.3 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 (Paragraph 5.3) and internal standard solution (Paragraph 5.4) to the syringe through the valve. (Surrogate spiking solution and internal standard solution may be mixed together.) The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 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 Paragraph 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample - grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked reagent 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, the procedures in Paragraphs 7.4.3.1.4 and 7.4.3.1.6 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.

7.4.3.1.7 Heat the sample to 40°C $\pm$ 1°C and purge the sample for 11.0 $\pm$ 0.1 min.

7.4.3.1.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Use 5 mL of the same reagent water as in the reagent blank. If saturated peaks occurred or would occur if a 1-g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils add 10 uL of the matrix spike solution (Paragraph 5.7) to the 5 mL of water (Paragraph 7.4.3.1.3). The concentration for a 5-g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 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. An aliquot of the extract is added to reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 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 waste 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 Paragraph 7.4.3.1.5. For waste that is soluble in methanol, 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 methanol into the vial and mark the bottom of the meniscus. Discard this solvent.)

7.4.3.2.2 Quickly add 9.0 mL of methanol; then add 1.0 mL of the surrogate spiking solution to the vial. Cap and shake for 2 min.

NOTE: Steps 7.4.3.2.1 and 7.4.3.2.2 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.

7.4.3.2.3 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 reagent methanol 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. The addition of a 100-uL aliquot of each of these extracts in Paragraph 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Paragraphs 7.4.1.2-7.4.1.4. This should be done prior to the addition of the methanol extract to reagent water.

7.4.3.2.5 Table 4 can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. If a screening procedure was followed (Method 3810 or 3820), 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 medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.4.3.2.6 Remove the plunger from a 5.0-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 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 uL of internal standard solution. Also add the volume of methanol extract determined in Paragraph 7.4.3.2.5 and a volume of methanol solvent to total 100 uL (excluding methanol in standards).

7.4.3.2.7 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.4.3.2.8 Proceed with the analysis as outlined in Paragraphs 7.4.1.11-7.4.1.16. Analyze all reagent blanks on the same instrument as that use for the samples. The standards and blanks should also contain 100 uL of methanol to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Paragraph 5.3), and 1.0 mL of matrix spike solution (Paragraph 5.7) as in Paragraph 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4-g sample. Add a 100-uL aliquot of this extract to 5 mL of water for purging (as per Paragraph 7.4.3.2.6).

TABLE 4. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF MEDIUM-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.

[a]The 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.

[b]Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

7.5 Data interpretation:

7.5.1 Qualitative analysis:

7.5.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as those of the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.5.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hr as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.5.1.1.2 (1) All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum). (2) The relative intensities of ions specified in (1) must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.5.1.2 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 ±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.

7.5.2 Quantitative analysis:

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.2.7).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

TABLE 5. VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromoform
Bromomethane	2-Butanone
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	2-Chloroethyl vinyl ether
Chloromethane	Dibromomethane
Dichlorodifluoromethane	1,4-Dichloro-2-butene
1,1-Dichloroethane	1,2-Dichloropropane
1,2-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	trans-1,3-Dichloropropene
1,1-Dichloroethene	1,1,1-Trichloroethane
trans-1,2-Dichloroethene	1,1,2-Trichloroethane
Iodomethane	Trichloroethene
Methylene chloride	Vinyl acetate
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Ethyl methacrylate
2-Hexanone
4-Methyl-2-pentanone
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylene

Sediment/Soil, Sludge, and Waste:

High-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = same as for water.

V_t = volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = volume of extract added (uL) for purging.

W_s = weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Paragraph 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all 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 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 water 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 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard 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 useable, 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.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Section 7.2.2.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.3.3 and the CCC criteria in 7.3.4, each 12 hr.

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

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. 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.

8.5.2 Prepare a QC check sample to contain 20 ug/L of each analyte by adding 200 uL of QC check sample concentrate to 100 mL of reagent water.

8.5.3 Four 5-mL aliquots of the well-mixed QC check sample are analyzed according to the method beginning in Section 7.4.1.

8.5.4 Calculate the average recovery ($\bar{X}$) in ug/L, and the standard deviation of the recovery (s) in ug/L, for each analyte using the four results.

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes 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 Table 6 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.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Paragraph 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, 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 Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

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

8.6.1.1 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 Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a specific limit, the spike should be at 20 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

TABLE 6. 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 (%)
Benzene	12.8-27.2	6.9	15.2-26.0	37-151
Bromodichloromethane	13.1-26.9	6.4	10.1-28.0	35-155
Bromoform	14.2-25.8	5.4	11.4-31.1	45-169
Bromomethane	2.8-37.2	17.9	D-41.2	D-242
Carbon tetrachloride	14.6-25.4	5.2	17.2-23.5	70-140
Chlorobenzene	13.2-26.8	6.3	16.4-27.4	37-160
2-Chloroethylvinyl ether	D-44.8	25.9	D-50.4	D-305
Chloroform	13.5-26.5	6.1	13.7-24.2	51-138
Chloromethane	D-40.8	19.8	D-45.9	D-273
Dibromochloromethane	13.5-26.5	6.1	13.8-26.6	53-149
1,2-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,3-Dichlorobenzene	14.6-25.4	5.5	17.0-28.8	59-156
1,4-Dichlorobenzene	12.6-27.4	7.1	11.8-34.7	18-190
1,1-Dichloroethane	14.5-25.5	5.1	14.2-28.4	59-155
1,2-Dichloroethane	13.6-26.4	6.0	14.3-27.4	49-155
1,1-Dichloroethene	10.1-29.9	9.1	3.7-42.3	D-234
trans-1,2-Dichloroethene	13.9-26.1	5.7	13.6-28.4	54-156
1,2-Dichloropropane	6.8-33.2	13.8	3.8-36.2	D-210
cis-1,3-Dichloropropene	4.8-35.2	15.8	1.0-39.0	D-227
trans-1,3-Dichloropropene	10.0-30.0	10.4	7.6-32.4	17-183
Ethyl benzene	11.8-28.2	7.5	17.4-26.7	37-162
Methylene chloride	12.1-27.9	7.4	D-41.0	D-221
1,1,2,2-Tetrachloroethane	12.1-27.9	7.4	13.5-27.2	46-157
Tetrachloroethene	14.7-25.3	5.0	17.0-26.6	64-148
Toluene	14.9-25.1	4.8	16.6-26.7	47-150
1,1,1-Trichloroethane	15.0-25.0	4.6	13.7-30.1	52-162
1,1,2-Trichloroethane	14.2-25.8	5.5	14.3-27.1	52-150
Trichloroethene	13.3-26.7	6.6	18.5-27.6	71-157
Trichlorofluoromethane	9.6-30.4	10.0	8.9-31.5	17-181
Vinyl chloride	0.8-39.2	20.0	D-43.5	D-251

Q = Concentration measured in QC check sample, in 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.
D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 624 and were calculated assuming a QC check sample concentration of 20 ug/L. These criteria are based directly upon the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.6.2 Analyze one 5-mL sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second 5-mL sample aliquot with 10 uL of the QC check 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.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be acounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 20 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, 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 Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as (100x'/T) $\pm$ 2.44(100S'/T)%.

8.6.4 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 Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Sectin 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, 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.

8.7.1 Prepare the QC check standard by adding 10 uL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 5 mL of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyze the QC check standard to determine the concentration measured (A) of each analyte. Calculate each precent recovery (p_s) as 100 (A/T)%, where T is the true value of the standard concentration.

TABLE 7. 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)
Benzene	0.93C+2.00	0.26$\bar{X}$-1.74	0.25$\bar{X}$-1.33
Bromodichloromethane	1.03C-1.58	0.15$\bar{X}$+0.59	0.20$\bar{X}$+1.13
Bromoform	1.18C-2.35	0.12$\bar{X}$+0.34	0.17$\bar{X}$+1.38
Bromomethane	1.00C	0.43$\bar{X}$	0.58$\bar{X}$
Carbon tetrachloride	1.10C-1.68	0.12$\bar{X}$+0.25	0.11$\bar{X}$+0.37
Chlorobenzene	0.98C+2.28	0.16$\bar{X}$-0.09	0.26$\bar{X}$-1.92
Chloroethane	1.18C+0.81	0.14$\bar{X}$+2.78	0.29$\bar{X}$+1.75
2-Chloroethylvinyl ether[a]	1.00C	0.62$\bar{X}$	0.84$\bar{X}$
Chloroform	0.93C+0.33	0.16$\bar{X}$+0.22	0.18$\bar{X}$+0.16
Chloromethane	1.03C-1.81	0.37$\bar{X}$+2.14	0.58$\bar{X}$+0.43
Dibromochloromethane	1.01C-0.03	0.17$\bar{X}$-0.18	0.17$\bar{X}$+0.49
1,2-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{X}$-1.45	0.30$\bar{X}$-1.20
1,3-Dichlorobenzene	1.06C+1.68	0.14$\bar{X}$-0.48	0.18$\bar{X}$-0.82
1,4-Dichlorobenzene[b]	0.94C+4.47	0.22$\bar{X}$-1.45	0.30$\bar{X}$-1.20
1,1-Dichloroethane	1.05C+0.36	0.13$\bar{X}$-0.05	0.16$\bar{X}$+0.47
1,2-Dichloroethane	1.02C+0.45	0.17$\bar{X}$-0.32	0.21$\bar{X}$-0.38
1,1-Dichloroethene	1.12C+0.61	0.17$\bar{X}$+1.06	0.43$\bar{X}$-0.22
trans-1,2,-Dichloroethene	1.05C+0.03	0.14$\bar{X}$+0.09	0.19$\bar{X}$+0.17
1,2-Dichloropropane[a]	1.00C	0.33$\bar{X}$	0.45$\bar{X}$
cis-1,3-Dichloropropene[a]	1.00C	0.38$\bar{X}$	0.52$\bar{X}$
trans-1,3-Dichloropropene[a]	1.00C	0.25$\bar{X}$	0.34$\bar{X}$
Ethyl benzene	0.98C+2.48	0.14$\bar{X}$+1.00	0.26$\bar{X}$-1.72
Methylene chloride	0.87C+1.88	0.15$\bar{X}$+1.07	0.32$\bar{X}$+4.00
1,1,2,2-Tetrachloroethane	0.93C+1.76	0.16$\bar{X}$+0.69	0.20$\bar{X}$+0.41
Tetrachloroethene	1.06C+0.60	0.13$\bar{X}$-0.18	0.16$\bar{X}$-0.45
Toluene	0.98C+2.03	0.15$\bar{X}$-0.71	0.22$\bar{X}$-1.71
1,1,1-Trichloroethane	1.06C+0.73	0.12$\bar{X}$-0.15	0.21$\bar{X}$-0.39
1,1,2-Trichloroethane	0.95C+1.71	0.14$\bar{X}$+0.02	0.18$\bar{X}$+0.00
Trichloroethene	1.04C+2.27	0.13$\bar{X}$+0.36	0.12$\bar{X}$+0.59
Trichlorofluoromethane	0.99C+0.39	0.33$\bar{X}$-1.48	0.34$\bar{X}$-0.39
Vinyl chloride	1.00C	0.48$\bar{X}$	0.65$\bar{X}$

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.

[a]Estimates based upon the performance in a single laboratory.
[b]Due to chromatographic resolution problems, performance statements for these isomers are based upon the sums of their concentrations.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 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.

8.8 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) as in Section 8.6, 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).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $p + 3s$
Lower Control Limit (LCL) = $p - 3s$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are 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.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene	86-115	74-121
1,2-Dichloroethane-d_4	76-114	70-121
Toluene-d_8	88-110	81-117

- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a 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 Table 1 were obtained using reagent water. Similar results were achieved using representative wastewaters. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 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 are presented in Table 7.

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, Method 624," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Bellar, T.A., and J.J. Lichtenberg, J. Amer. Water Works Assoc., 66(12), 739-744, 1974.

4. 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.

5. Budde, W.L. and J.W. Eichelberger, "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories," EPA-600/4-79-020, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, April 1980.

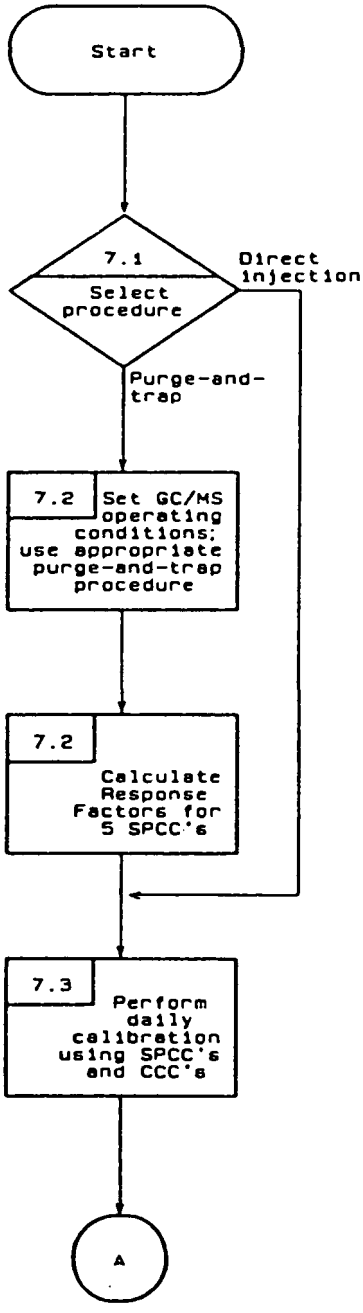
6. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

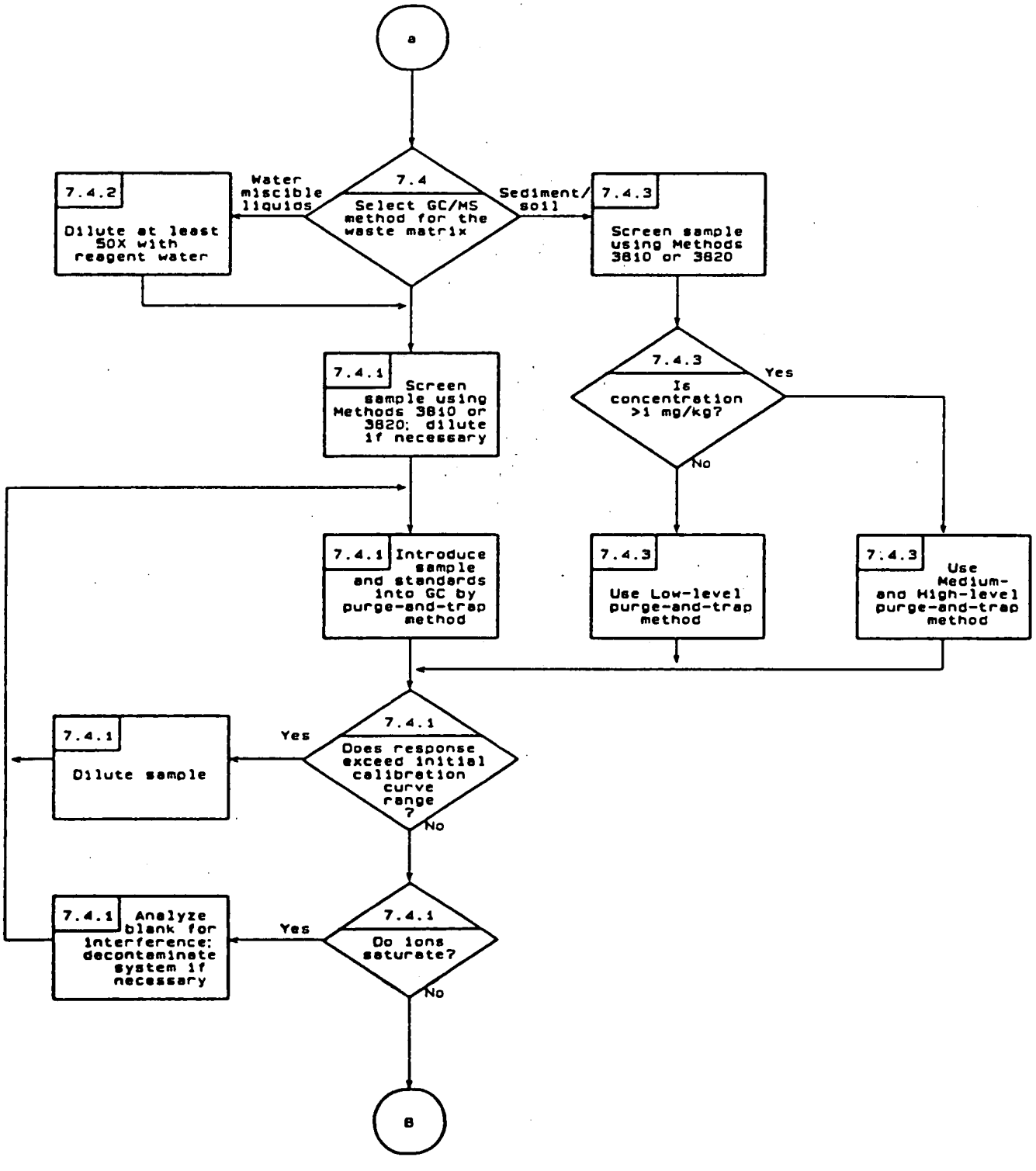
7. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

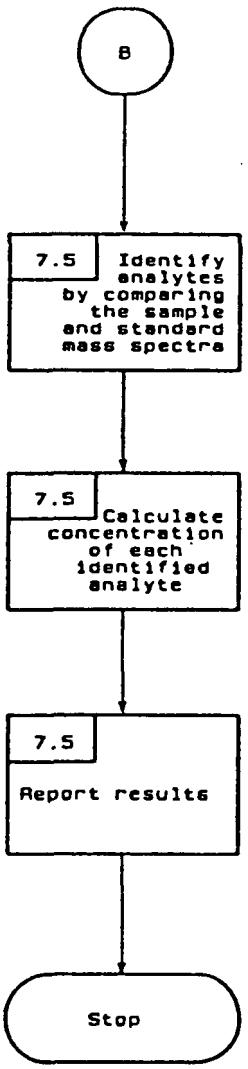
8. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

9. "Interlaboratory Method Study for EPA Method 624-Purgeables," Final Report for EPA Contract 68-03-3102.

10. "Method Performance Data for Method 624," Memorandum from R. Slater and T. Pressley, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, January 17, 1984.


Start
7.1
Select procedure
Direct injection
Purge-and-trap
7.2
Set GC/MS operating conditions; use appropriate purge-and-trap procedure
7.2
Calculate Response Factors for 5 SPCC's
7.3
Perform daily calibration using SPCC's and CCC's
A


A
7.4
Select GC/MS method for the waste matrix
Water miscible liquids
Sediment/ soil
7.4.2
Dilute at least 50X with reagent water
7.4.3
Screen sample using Methods 3810 or 3820
7.4.1
Screen sample using Methods 3810 or 3820; dilute if necessary
7.4.3
Is concentration >1 mg/kg?
Yes
No
7.4.1
Introduce sample and standards into GC by purge-and-trap method
7.4.3
Use Low-level purge-and-trap method
7.4.3
Use Medium- and High-level purge-and-trap method
7.4.1
Does response exceed initial calibration curve range ?
Yes
No
7.4.1
Dilute sample
7.4.1
Do ions saturate?
Yes
No
7.4.1
Analyze blank for interference; decontaminate system if necessary
B


B
7.5
Identify analytes by comparing the sample and standard mass spectra
7.5
Calculate concentration of each identified analyte
7.5
Report results
Stop

METHOD 8250

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: PACKED COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8250 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8250 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic packed column. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected and are not being determined by Method 8080. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8250 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHROMATOGRAPHIC CONDITIONS, METHOD DETECTION LIMITS, AND CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Acenaphthene	17.8	1.9	154	153, 152
Acenaphthene-d_{10} (I.S.)	--	--	164	162, 160
Acenaphthylene	17.4	3.5	152	151, 153
Acetophenone	--	--	105	77, 51
Aldrin	24.0	1.9	66	263, 220
Aniline	--	--	93	66, 65
Anthracene	22.8	1.9	178	176, 179
4-Aminobiphenyl	--	--	169	168, 170
Aroclor-1016[b]	18-30	--	222	260, 292
Aroclor-1221[b]	15-30	30	190	224, 260
Aroclor-1232[b]	15-32	--	190	224, 260
Aroclor-1242[b]	15-32	--	222	256, 292
Aroclor-1248[b]	12-34	--	292	362, 326
Aroclor-1254[b]	22-34	36	292	362, 326
Aroclor-1260[b]	23-32	--	360	362, 394
Benzidine[a]	28.8	44	184	92, 185
Benzoic acid	--	--	122	105, 77
Benzo(a)anthracene	31.5	7.8	228	229, 226
Benzo(b)fluoranthene	34.9	4.8	252	253, 125
Benzo(k)fluoranthene	34.9	2.5	252	253, 125
Benzo(g,h,i)perylene	45.1	4.1	276	138, 277
Benzo(a)pyrene	36.4	2.5	252	253, 125
Benzyl alcohol	--	--	108	79, 77
α-BHC[a]	21.1	--	183	181, 109
β-BHC	23.4	4.2	181	183, 109
δ-BHC	23.7	3.1	183	181, 109
γ-BHC (Lindane)[a]	22.4	--	183	181, 109
Bis(2-chloroethoxy)methane	12.2	5.3	93	95, 123
Bis(2-chloroethyl)ether	8.4	5.7	93	63, 95
Bis(2-chloroisopropyl)ether	9.3	5.7	45	77, 121
Bis(2-ethylhexyl)phthalate	30.6	2.5	149	167, 279
4-Bromophenyl phenyl ether	21.2	1.9	248	250, 141
Butyl benzyl phthalate	29.9	2.5	149	91, 206
Chlordane[b]	19-30	--	373	375, 377
4-Chloroaniline	--	--	127	129
1-Chloronaphthalene	--	--	162	127, 164
2-Chloronaphthalene	15.9	1.9	162	127, 164
4-Chloro-3-methylphenol	13.2	3.0	107	144, 142
2-Chlorophenol	5.9	3.3	128	64, 130
4-Chlorophenyl phenyl ether	19.5	4.2	204	206, 141
Chrysene	31.5	2.5	228	226, 229
Chrysene-d_{12} (I.S.)	--	--	240	120, 236
4,4'-DDD	28.6	2.8	235	237, 165
4,4'-DDE	27.2	5.6	246	248, 176

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
4,4'-DDT	29.3	4.7	235	237, 165
Dibenz(a,j)acridine	--	--	279	280, 277
Dibenz(a,h)anthracene	43.2	2.5	278	139, 279
Dibenzofuran	--	--	168	139
Di-n-butylphthalate	24.7	2.5	149	150, 104
1,3-Dichlorobenzene	7.4	1.9	146	148, 111
1,4-Dichlorobenzene	7.8	4.4	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	--	--	152	150, 115
1,2-Dichlorobenzene	8.4	1.9	146	148, 111
3,3'-Dichlorobenzidine	32.2	16.5	252	254, 126
2,4-Dichlorophenol	9.8	2.7	162	164, 98
2,6-Dichlorophenol	--	--	162	164, 98
Dieldrin	27.2	2.5	79	263, 279
Diethylphthalate	20.1	1.9	149	177, 150
p-Dimethylaminoazobenzene	--	--	120	225, 77
7,12-Dimethylbenz(a)anthracene	--	--	256	241, 257
α-,α-Dimethylphenethylamine	--	--	58	91, 42
2,4-Dimethylphenol	9.4	2.7	122	107, 121
Dimethylphthalate	18.3	1.6	163	194, 164
4,6-Dinitro-2-methylphenol	16.2	24	198	51, 105
2,4-Dinitrophenol	15.9	42	184	63, 154
2,4-Dinitrotoluene	19.8	5.7	165	63, 89
2,6-Dinitrotoluene	18.7	1.9	165	63, 89
Diphenylamine	--	--	169	168, 167
1,2-Diphenylhydrazine	--	--	77	105, 182
Di-n-octylphthalate	32.5	2.5	149	167, 43
Endosulfan I[a]	26.4	--	195	339, 341
Endosulfan II[a]	28.6	--	337	339, 341
Endosulfan sulfate	29.8	5.6	272	387, 422
Endrin[a]	27.9	--	263	82, 81
Endrin aldehyde	--	--	67	345, 250
Endrin ketone	--	--	317	67, 319
Ethyl methanesulfonate	--	--	79	109, 97
Fluoranthene	26.5	2.2	202	101, 203
Fluorene	19.5	1.9	166	165, 167
2-Fluorobiphenyl (surr.)	--	--	172	171
2-Fluorophenol (surr.)	--	--	112	64
Heptachlor	23.4	1.9	100	272, 274
Heptachlor epoxide	25.6	2.2	353	355, 351
Hexachlorobenzene	21.0	1.9	284	142, 249
Hexachlorobutadiene	11.4	0.9	225	223, 227
Hexachlorocyclopentadiene[a]	13.9	--	237	235, 272
Hexachloroethane	8.4	1.6	117	201, 199
Indeno(1,2,3-cd)pyrene	42.7	3.7	276	138, 227

TABLE 1. - Continued

Compound	Retention Time (min)	Method detection limit (ug/L)	Primary Ion	Secondary Ion(s)
Isophorone	11.9	2.2	82	95, 138
Methoxychlor	--	--	227	228
3-Methylcholanthrene	--	--	268	253, 267
Methyl methanesulfonate	--	--	80	79, 65
2-Methylnaphthalene	--	--	142	141
2-Methylphenol	--	--	108	107, 79
4-Methylphenol	--	--	108	107, 79
Naphthalene	12.1	1.6	128	129, 127
Naphthalene-d_8 (I.S.)	--	--	136	68
1-Naphthylamine	--	--	143	115, 116
2-Naphthylamine	--	--	143	115, 116
2-Nitroaniline	--	--	65	92, 138
3-Nitroaniline	--	--	138	108, 92
4-Nitroaniline	--	--	138	108, 92
Nitrobenzene	11.1	1.9	77	123, 65
Nitrobenzene-d_5 (surr.)	--	--	82	128, 54
2-Nitrophenol	6.5	3.6	139	109, 65
4-Nitrophenol	20.3	2.4	139	109, 65
N-Nitroso-di-n-butylamine	--	--	84	57, 41
N-Nitrosodimethylamine[a]	--	--	42	74, 44
N-Nitrosodiphenylamine[a]	20.5	1.9	169	168, 167
N-Nitroso-di-N-propylamine	--	--	70	130, 42
N-Nitrosopiperidine	--	--	42	114, 55
Pentachlorobenzene	--	--	250	252, 248
Pentachloronitrobenzene	--	--	295	237, 142
Pentachlorophenol	17.5	3.6	266	264, 268
Perylene-d_{12} (I.S.)	--	--	264	260, 265
Phenacetin	--	--	108	109, 179
Phenanthrene	22.8	5.4	178	179, 176
Phenanthrene-d_{10} (I.S.)	--	--	188	94, 80
Phenol	8.0	1.5	94	65, 66
Phenol-d_6 (surr.)	--	--	99	42, 71
2-Picoline	--	--	93	66, 92
Pronamide	--	--	173	175, 145
Pyrene	27.3	1.9	202	200, 203
Terphenyl-d_{14} (surr.)	--	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	--	--	216	214, 218
2,3,4,6-Tetrachlorophenol	--	--	232	230, 131
2,4,6-Tribromophenol (surr.)	--	--	330	332, 141
1,2,4-Trichlorobenzene	11.6	1.9	180	182, 145
2,4,5-Trichlorophenol	--	--	196	198, 200
2,4,6-Trichlorophenol	11.8	2.7	196	198, 200
Toxaphene[b]	25-34	--	159	231, 233

[a]See Section 1.3
[b]These compounds are mixtures of various isomers.

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

[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.

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level 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/mass spectrometer system:

4.1.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases.

4.1.2 **Columns:**

4.1.2.1 For base/neutral compound detection: 2-m x 2-mm I.D. stainless or glass, packed with 3% SP-2250-DB on 100/120 mesh Supelcoport or equivalent.

4.1.2.2 For acid compound detection: 2-m x 2-mm I.D. glass, packed with 1% SP-1240-DA on 100/120 mesh Supelcoport or equivalent.

4.1.3 **Mass spectrometer:** Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA [a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a] J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

used. GC-to-MS interfaces constructed entirely of glass or glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.1.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide.

Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/ul. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. 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). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

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 preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 **Direct injection:** In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Electron energy: 70 volts (nominal)
Mass range: 35-500 amu
Scan time: 1 sec/scan
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Helium at 30 mL/min

Conditions for base/neutral analysis (3% SP-2250-DB):

Initial column temperature and hold time: 50°C for 4 min
Column temperature program: 50-300°C at 8°C/min
Final column temperature hold: 300°C for 20 min

Conditions for acid analysis (1% SP-1240-DA):

Initial column temperature and hold time: 70°C for 2 min
Column temperature program: 70-200°C at 8°C/min
Final column temperature hold: 200°C for 20 min

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Calculate response factors (RFs) for each compound 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_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average response factors are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average RF for these is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds** (SPCCs): A system performance check must be made during every 12 hr shift. 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 met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-Octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect these criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using the appropriate column (as specified in Paragraph 4.1.2). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 Qualitative analysis:

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference compounds should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 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 (e.g., for EPA Contract Laboratory Program requirements, up to 20 substances of greatest apparent concentration not listed in the Hazardous Substance List must be tentatively identified). 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 spectra with the nearest library searches will

the mass spectral interpretation specialist assign a tentative identification. 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 ±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 sample the 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.

7.6.2 **Quantitative analysis:**

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

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 water 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 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard 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.

8.4 Required instrument QC is found in the following section:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

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

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. 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.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

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

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all 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 Table 6 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 analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

8.5.6.2 Beginning with Section 8.5.2, 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 Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

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

8.6.1.1 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

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitroso-di-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check 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.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, 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 Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{X}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 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 Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory.

TABLE 7. 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)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitroso-di-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in 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.

If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, 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.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard 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.

8.7.3 Compare the percent recovery (P_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 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.

8.8 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) as in Section 8.6, 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).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are 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."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or mass spectrometry using other ionization modes 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 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and 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 7.

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, Method 625," October 26, 1984.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

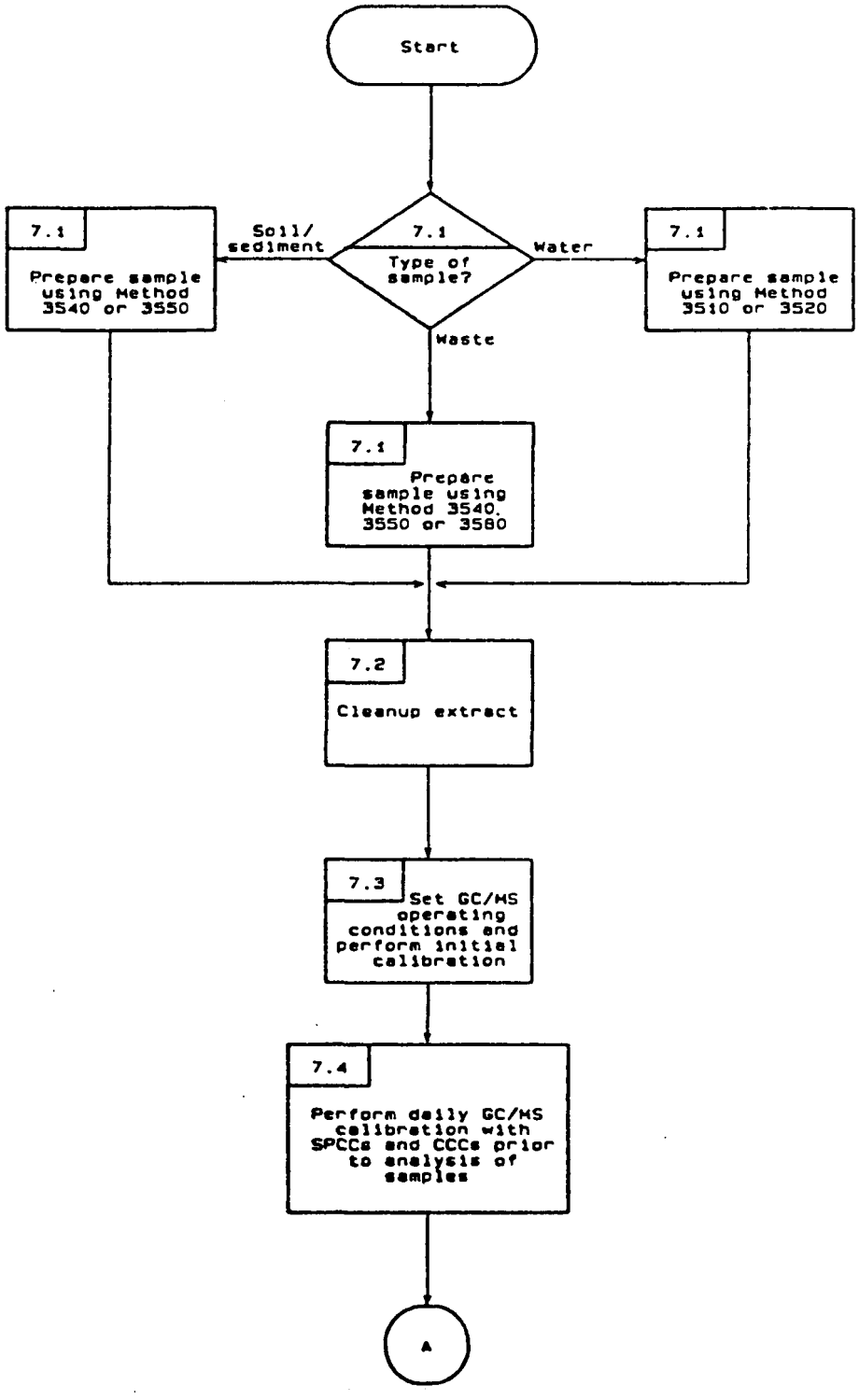
3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

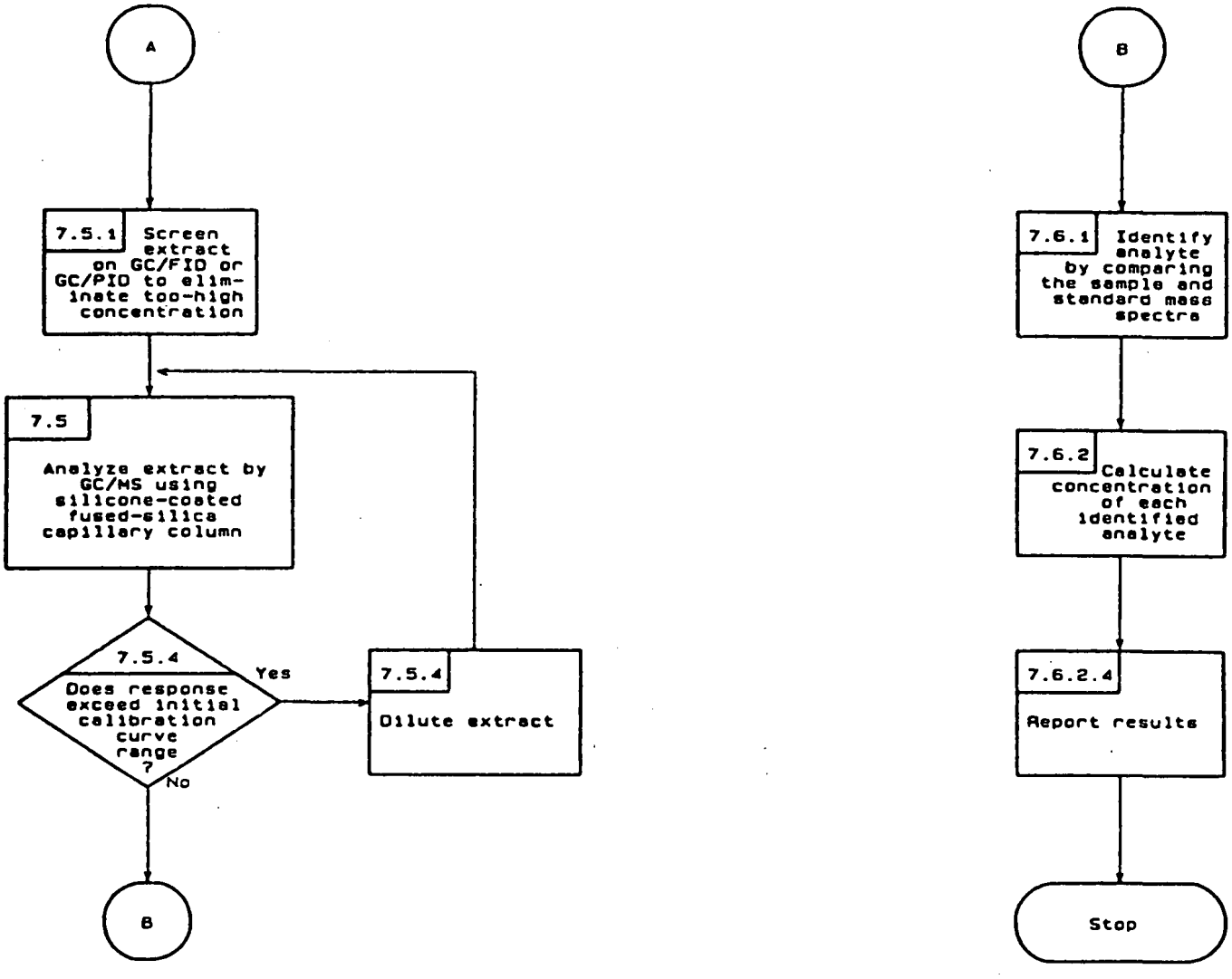
4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.


Start
7.1
Type of sample?
Soil/ sediment
Water
Waste
7.1
Prepare sample using Method 3540 or 3550
7.1
Prepare sample using Method 3510 or 3520
7.1
Prepare sample using Method 3540, 3550 or 3580
7.2
Cleanup extract
7.3
Set GC/MS operating conditions and perform initial calibration
7.4
Perform daily GC/MS calibration with SPCCs and CCCs prior to analysis of samples
A


A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
No
7.5.4 Dilute extract
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop

METHOD 8260

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR VOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

DRAFT

1.0 SCOPE AND APPLICATION

1.1 Method 8260 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]
Benzene	71-43-2
Bromobenzene	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Bromomethane	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroethane	75-00-3
Chloroform	67-66-3
Chloromethane	74-87-3
2-Chlorotoluene	95-49-8
4-Chlorotoluene	106-43-4
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane	74-95-3
1,2-Dichlorobenzene	95-50-1
1,3-Dichlorobenzene	541-73-1
1,4-Dichlorobenzene	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane	75-34-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethene	75-35-4
cis-1,2-Dichloroethene	156-69-4
trans-1,2-Dichloroethene	156-60-5
1,2-Dichloropropane	78-87-5
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
Ethylbenzene	100-41-4
Hexachlorobutadiene	87-68-3

Analyte	CAS No.[a]
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
Methylene chloride	75-09-2
Naphthalene	91-20-3
n-Propylbenzene	103-65-1
Styrene	100-42-5
1,1,1,2-Tetrachloroethane	630-20-6
1,1,2,2,-Tetrachloroethane	79-34-5
Tetrachloroethene	127-18-4
Toluene	108-88-3
1,2.3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene	120-82-1
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-Trichloropopane	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride	75-01-4
o-Xylene	95-47-6
m-Xylene	108-38-3
p-Xylene	106-42-3

[a]Chemical Abstract Services Registry Number.

1.2 Method 8260 can be used to quantify most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for lists of analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented.

1.3 The practical quantitation limit (PQL) of Method 8260 for an individual compound is approximately 5 ug/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 ug/L for ground water (see Table 3). PQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 Method 8260 is based upon a purge-and-trap, gas chromatographic/ mass spectrometric (GC/MS) procedure. This method is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed diretly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for anaylsis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

2.2 If the above sample introduction techniques are not applicable, a portion of the sample is dispersed in solvent to dissolve the volatile organic constituents. A portion of the solution is combined with water in the purge chamber. It is then analyzed by purge-and-trap GC/MS following the normal water method.

2.3 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantified by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter (Figure 1). Subtracting blank values from sample results is not permitted. If reporting values not corrected for blanks result in what the laboratory feels is a false positive for a sample, this should be fully explained in text accompanying the uncorrected data.

3.2 Interfering contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds or high levels of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with water, and then dry the purging device in an oven at 105°C. In extreme situations, the whole purge and trap device may require dismantling and

cleaning. Screening of the samples prior to purge and trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.3 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

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

4.0 APPARATUS AND MATERIALS

4.1 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.

4.1.1 The recommended purging chamber is designed to accept 5 mL (and 25 mL if the lowest detection limit is required) 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 (i.e. needle spargers), may be utilized, provided equivalent performance is demonstrated.

4.1.2 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 absorbents: 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 Figure 2). 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 room, 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. Traps normally last 2-3 months when used daily. Some signs of a deteriorating trap are: uncharaceristic recoveries of surrogates, especially toluene-d_8; a loss of the response of the internal standards during a 12 hour shift; and/or a rise in the baseline in the early portion of the scan.

4.1.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The trap bake-out temperature should not exceed 220°C. The desorber design illustrated in Figure 2 meets these criteria.

4.1.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 3 and 4.

4.1.5 Trap Packing Materials

4.1.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

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

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

4.1.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26 lot #M-2649 by crushing through a 26 mesh screen.

4.2 Heater or heated oil bath - Should be capable of maintaining the purging chamber to within 1°C over the temperature range of ambient to 100°C.

4.3 Gas chromatography/mass spectrometer/data system

4.3.1 The GC must be capable of temperature programming and should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation. For some column configuration, the column oven must be cooled to < 30°C, therefore, a subambient oven controller may be required. The GC is interfaced to the MS with an all glass enrichment device and an all glass transfer line, but any enrichment device or transfer line can be used if the performance specifications described in Step 8.2.4 can be achieved.

4.3.2 Gas chromatographic column 1 - 60 m x 0.75 mm i.d. VOCOL (Supelco) wide bore capillary column with 1.5 um film thickness. The flow rate of helium carrier gas is established at 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min, and held until all expected compounds have eluted. A sample chromatogram obtained with this column is presented in Figure 5.

4.3.3 Gas chromatographic column 2 - 30 m x 0.53 mm i.d. DB-624 wide-bore (J&W Scientific) column with 3 um film thickness.

4.3.3.1 Cryogenic cooling - Helium carrier gas flow is 15 mL/min. The column temperature is held for 5 minutes at 10°C, then programmed to 160°C at 6°C/min. A sample chromatogram obtained with this column is presented in Figure 6.

4.3.3.2 Non-cryogenic cooling - It is recommended that carrier gas flow and split and make-up gases be set using performance of standards as guidance. Set the carrier gas head pressure to 10 psi and the split to 30 mL/min. Optimize the make-up gas flow for the separator (approximately 30 mL/min) by injecting BFB and determining the optimum response when varying the make-up gas. This will require several injections of BFB. Next, make several injections of the volatile working standard with all analytes of interst. Adjust the carrier and split to provide optimum chromatography and response. This is an especially critical adjustment for the volatile gas analytes. The head pressure should optimize between 8-12 psi and the split between 20-60 mL/min. The use of the splitter is important to minimize the effect of water on analyte response; to allow the use of a larger volume of helium during trap desorption; and to slow column flow. The column temperature is held for 2 minutes at 45°C, then programmed to 200°C at 8°C/min, and held for 6 minutes. A sample chromatogram is presented in Figure 7. A trap preheated to 150°C prior to trap desorption is required to provide adequate chromatography of the gas analytes.

4.3.4 Gas chromatographic column 3 - 30 m x 0.32 mm i.d. fused silica capillary column coated with Durabond DB-5 (J&W Scientific) with a 1 um film thickness. Helium carrier gas flow is 4 mL/min. The column is maintained at 10°C for 5 minutes, then programmed at 6°C/min for 10 minutes then 15°C/min for 5 minutes to 145°C. A sample chromatogram obtained with this column is presented in Figure 8.

4.3.5 Mass spectrometer - Mass spectral data are obtained with electron impact ionization at a nominal electron energy of 70 eV. The mass spectrometer must be capable of scanning from 35 to 300 amu every 2 seconds or less and must produce a mass spectrum that meets all criteria in Table 4 when 50 ng of 4-bromofluorobenzene is introduced into the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC. Injector temperature should be 200-225°C and transfer line temperature, 250-300°C. This includes, but is not limited to quadrupole, magnetic, ion trap, time of fight, and mixed analyzer (i.e. combined analyzers such as magnetic and quadrupole) mass spectrometers.

4.3.6 GC/MS interface - Any GC-to-MS interface that gives acceptable calibration points at 50 ng or less per injection for each of the analytes and achieves all acceptable performance criteria (see Table 4) may be used. GC-to-MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass can be deactivated by silanizing with dichlorodimethylsilane. This interface is only needed for the wide bore columns ($\geq$ 0.53 mm i.d.).

4.3.7 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 GC/MS 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 integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the NBS/EPA Mass Spectral Library should also be available.

4.4 Capillary precolumn interface when using cryogenic cooling - This device interfaces the purge and trap concentrator to the capillary gas chromatograph. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused silica capillary precolumn. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.4.1 Under a stream of liquid nitgrogen, the temperature of the fused silica in the interface is maintained at -150°C during the cryofocussing step. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.5 Microsyringes - 10, 25, 100, 250, 500, and 1,000-uL.

4.6 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.7 Syringes - 5, 10, or 25-mL, gas-tight with shutoff valve.

4.8 Balance - Analytical, capable of accurately weighing 0.0001 g, and a top-loading balance capable of weighing 0.1 g.

4.9 Glass scintillation vials - 20-mL, with Teflon lined screw-caps or glass culture tubes with Teflon lined screw-caps.

4.10 Vials - 2-mL, for GC autosampler.

4.11 Disposable pipets - Pasteur.

5.0 REAGENTS

5.1 Methanol, CH_3OH. Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.2 Reagent Tetraglyme - Reagent tetraglyme is defined as tetraglyme in which interference is not observed at the method detection limit of compounds of interest.

CAUTION: Glycolethers are suspected carcinogens. All solvent handling should be done in a hood while using proper protective equipment to minimize exposure to liquid and vapor.

5.2.1 Tetraglyme (tetraethylene glycol dimethyl ether, Aldrich #17, 240-5 or equivalent), $C_8H_{18}O_5$. 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).

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 a 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.

5.2.2 In order to demonstrate that all interfering volatiles have been removed from the tetraglyme, a water/tetraglyme blank must be analyzed.

5.3 Polyethylene glycol, reagent grade. Free of interferences at the detection limit of the analytes.

5.4 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.

5.5 Hydrochloric acid (1:1), HCL. Carefully add a measured volume of concentrated HCL to an equal volume of water.

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 interferents 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 450 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 solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 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.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-uL 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.

5.7.2.2 Gasses - To prepare standards for any compounds that boil below 30°C (e.g. bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared 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.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in micrograms per microliter (ug/uL) from the net gain in weight. When compound purity is assayed to be 90% 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.

5.7.4 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.

5.7.5 Prepare fresh standards for gases every two months or sooner if comparison with check standards indicates a problem. Reactive compounds such as 2-chloroethylvinyl ether and 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. 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.

5.8 Secondary dilution standards - Using stock standard solutions, prepare in 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. Store in a vial with no headspace for one week only.

5.9 Surrogate standards - The surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described in Step 5.7, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 ug/10 mL in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 uL of the surrogate spiking solution prior to analysis.

5.10 Internal standards - The recommended internal standards are chlorobenzene-d_5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d_4, and pentafluorobenzene. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Steps 5.7 and 5.8. It is recommended that the secondary dilution standard should be prepared at a concentration of 25 ug/mL of each internal standard compound. Addition of 10 uL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 ug/L.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/uL of BFB in methanol should be prepared.

5.12 Calibration standards - Calibration standards at a minimum of five concentration levels should be prepared from the secondary dilution of stock standards (see Steps 5.7 and 5.8). Prepare these solutions in water. 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 but should not exceed the working range of the GC/MS system. 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). Calibration standards must be prepared daily.

5.13 Matrix spiking standards - Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. It is desirable to perform a matrix spike using compounds found in samples. Some permits may require spiking specific compounds of interest, especially if they are polar and would not be represented by the above listed compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 ug/10.0 mL.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C to -20°C in amber bottles with Teflon lined screw-caps.

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 Direct injection - In very limited appliations (e.g. aqueous process wastes) direct injection of the sample into the GC/MS 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 using the same solvent (e.g. water) for standards as the sample matrix (bypassing the purge-and-trap device).

7.2 Initial calibration for purge-and-trap procedure

7.2.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 50 ng injection or purging of 4-bromofluorobenzene (2 uL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.2.2 Assemble a purge-and-trap device that meets the specification in Step 4.1. 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.

7.2.3 Connect the purge-and-trap device to a gas chromatograph.

7.2.4 A set of at least five calibration standards containing the method analytes is needed. One calibration standard should contain each analyte at a concentration approaching but greater than the method detection limit (Table 1) for that compound; the other calibration standards should contain analytes at concentrations that define the range of the method. The purging efficiency for 5 mL of water is greater than for 25 mL, therefore, develop the standard curve with whichever volume of sample that will be analyzed. To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 uL of internal standard. Then transfer the contents to a purging device.

7.2.5 Carry out the purge-and-trap analysis procedure as described in Step 7.4.1.

7.2.6 Tabulate the area response of the characteristic ions (see Table 5) against concentration for each compound and each internal standard. Calculate response factors (RF) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RF for a compound should be the internal standard that has a retention time closest to the compound being measured (Step 7.5.2). 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.

7.2.7 The average RF must be calculated for each compound and recorded on Form VI (see Chapter One). A system performance check should be made before this 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 occurences are:

7.2.7.1 Chloromethane - This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.7.2 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. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.2.7.3 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.

7.2.8 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for Calibration Check Compounds (CCCs). Record the %RSDs for all compounds on Form VI (see Chapter One). The percent RSD is calculated as follows:

$$\%RSD = \frac{SD}{\bar{x}} \; 13 \times 100$$

where:

RSD = Relative standard deviation.

$\bar{x}$ = Mean of 5 initial RFs for a compound.

SD = Standard deviation of average RFs for a compound.

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

The %RSD for each individual CCC must be less than 30 percent. This criterion must be met for the individual calibration to be valid. The CCCs are:

1,1-Dichloroethene,
Chloroform,
1,2-Dichloropropane,
Toluene,
Ethylbenzene, and
Vinyl chloride.

If the CCCs are not required analytes by the permit, then all required analytes must meet the 30% RSD criterion.

7.3 Daily GC/MS calibration

7.3.1 Prior to the analysis of samples, inject or purge 50-ng of the 4-bromofluorobenzene standard. The resultant mass spectra for the BFB must meet all of the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift.

7.3.2 The initial calibration curve (Step 7.2) for each compound of interest must be checked and verified once every 12 hours of analysis time. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC (Step 7.3.3) and CCC (Step 7.3.4).

7.3.3 System Performance Check Compounds (SPCCs) - A system performance check must be made each 12 hours. 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 met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum response factor for volatile SPCCs is 0.300 (0.250 for Bromoform). Some possible problems are standard mixture degration, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system.

7.3.4 Calibration Check Compounds (CCCs) - After the system performance check is met, CCCs listed in Step 7.2.8 are used to check the validity of the initial calibration. Calculate the percent difference using the following equation:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_c}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = Average response factor from initial calibration.

RF_c = Response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 25%, the initial calibration is assumed to be valid. If the criterion is not met (> 25% difference), for any one CCC, corrective action must be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration must be generated. This criterion must be met before quantitative sample analysis begins. If the CCCs are not required analytes by the permit, then all required analytes must meet the 25% difference criterion.

7.3.5 The 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 hours), the chromatograhic system must be inspected for malfunctions and corections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning are necessary.

7.4 GC/MS analysis

7.4.1 Water samples

7.4.1.1 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 used are the headspace sampler (Method 3810) using 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 and analysis of the extract on a GC with a FID and/or an ECD (Method 3820).

7.4.1.2 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.4.1.3 Set up the GC/MS system as outlined in Step 4.3.

7.4.1.4 BFB tuning criteria and daily GC/MS calibration criteria must be met (Step 7.3) before analyzing samples.

7.4.1.5 Adjust the purge gas (helium) flow rate to 25-40 mL/min 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 (see Step 7.2.7).

7.4.1.6 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25-mL syringe. 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.

7.4.1.7 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.

7.4.1.7.1 Dilutions may be made in volumetric flasks (10 to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.4.1.7.2 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.

7.4.1.7.3 Inject the proper aliquot of samples from the syringe prepared in Step 7.4.1.6 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.4.1.7.4 Fill a 5-mL syringe with the diluted sample as in Step 7.4.1.6.

7.4.1.8. Compositing samples prior to GC/MS analysis

7.4.1.8.1 Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.

7.4.1.8.2 The samples must be cooled at 4°C during this step to minimize volatilization losses.

7.4.1.8.3 Mix well and draw out a 5 mL aliquot for analysis.

7.4.1.8.4 Follow sample introduction, purging, and desorption steps described in the method.

7.4.1.8.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used unless a 25 mL sample is to be purged.

7.4.1.9 Add 10.0 uL of surrogate spiking solution (Step 5.9) and 10 uL of internal standard spiking solution (Step 5.10) 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. The addition of 10 uL of the surrogate spiking solution to 5 mL of sample is equivalent to a concentration of 50 ug/L of each surrogate standard.

7.4.1.10 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.

7.4.1.11 Close both valves and purge the sample for 11.0 ± 0.1 minutes at ambient temperature. Be sure the trap is cooler than 25°C.

7.4.1.12 Sample desorption - The mode of sample desorption is determined by the type of capillary column employed for the analysis. When using a wide bore capillary column, follow the desorption conditions of Step 7.4.1.13. The conditions for using narrow bore columns are described in Step 7.4.1.14.

7.4.1.13 Sample desorption for wide bore capillary column. Under most conditions, this type of column must be interfaced to the MS through an all glass jet separator.

7.4.1.13.1 After the 11 minute purge, attach the trap to the chromatograph, adjust the purge and trap system to the desorb mode (Figure 4) and initiate the temperature program sequence of the gas chromatograph and start data acquisition. Introduce the trapped materials to the GC column by rapidly

heating the trap to 180°C while backflushing the trap with an inert gas at 15 mL/min for 4 minutes. If the non-cryogenic cooling technique is followed, the trap must be preheated to 150°C just prior to trap desorption at 180°C. While the purged analytes are being introduced into the gas chromatograph, empty the purging device using the sample syringe and wash the chamber with two 5 or 25 mL portions of water depending on the size of the purge device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle.

7.4.1.13.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 160°C and hold until all analytes elute.

7.4.1.13.3 After desorbing the sample for 4 minutes, condition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 7 minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When the trap is cool, the next sample can be analyzed.

7.4.1.14 Sample desorption for narrow bore capillary column. Under normal operating conditions, most narrow bore capillary columns can be interfaced directly to the MS without a jet separator.

7.4.1.14.1 After the 11 minute purge, attach the trap to the cryogenically cooled interface at -150°C and adjust the purge-and-trap system to the desorb mode (Figure 4). Introduce the trapped materials to the interface by rapidly heating the trap to 180°C while backflushing the trap with an inert gas at 4 mL/min for 5 minutes. While the extracted sample is being introduced into the interface, empty the purging device using the sample syringe and rinse the chamber with two 5 or 25 mL portions of water depending on the size of the purging device. After the purging device has been emptied, leave the syringe valve open to allow the purge gas to vent through the sample introduction needle. After desorbing for 5 minutes, flash heat the interface to 250°C and quickly introduce the sample on the chromatographic column. Start the temperature program sequence, and initiate data acquisition.

7.4.1.14.2 Hold the column temperature at 10°C for 5 minutes, then program at 6°C/min to 70°C and then at 15°C/min to 145°C. After desorbing the sample for 5 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately 15 minutes, turn off the trap heater and open the syringe valve to stop the gas

flow through the trap. When the trap is cool, the next sample can be analyzed.

7.4.1.15 If the initial analysis of the 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. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion. When a sample is analyzed that has saturated ions 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.

7.4.1.16 For matrix spike analysis, add 10 uL of the matrix spike solution (Step 5.13) to the 5 mL of sample purged. Disregarding any dilutions, this is equivalent to a concentration of 50 ug/L of each matrix spike standard.

7.4.1.17 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 Steps 7.5.1 and 7.5.2 for qualitative and quantitative analysis.

7.4.2 Water-miscible liquids

7.4.2.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with water.

7.4.2.2 Initial and serial dilutions can be prepared by pipeting 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.

7.4.2.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with water by adding at least 20 uL, but not more than 100-uL of liquid sample. The sample is ready for addition of internal and surrogate standards.

7.4.3 Sediment/soil and waste samples - It is highly recommended that all samples of this type be screened prior to the purge-and-trap GC/MS analysis. The headspace method (Method 3810) or the hexadecane extraction and screening method (Method 3820) may used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. 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).

7.4.3.1 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 internal standards. Analyze all blanks and standards under the same conditions as the samples. See Figure 9 for an illustration of a low soils impinger.

7.4.3.1.1 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.

7.4.3.1.2 The GC/MS system should be set up as in Steps 7.4.1.3-7.4.1.4. 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.

7.4.3.1.3 Remove the plunger from a 5-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 5.0 mL. Add 10 uL each of surrogate spiking solution (Step 5.9) and internal standard solution (Step 5.10) to the syringe through the valve (surrogate spiking solution and internal standard solution may be mixed together). The addition of 10 uL of the surrogate spiking solution to 5 g of sediment/soil is equivalent to 50 ug/kg of each surrogate standard.

7.4.3.1.4 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 7.4.3.1.1 into a tared purge device. Note and record the actual weight to the nearest 0.1 g.

7.4.3.1.5 Determine the percent moisture of the soil/sediment sample. This includes waste samples that are amenable to moisture determination. Other wastes should be reported on a wet-weight basis. Immediately after weighing the sample, weigh (to 0.1 g) 5-10 g of additional sediment/soil into a tared crucible. Dry the contents of the crucibles overnight at 105°C. Allow to cool in a desiccator and reweigh the dried contents. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\% \text{ moisture} = \frac{\text{grams of sample} - \text{grams of dry sample}}{\text{grams of sample}} \times 100$$

7.4.3.1.6 Add the spiked water to the purging device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

that has stringent control of

NOTE: Prior to the attachment of the purge device, the procedures in Steps 7.4.3.1.4 and 7.4.3.1.6 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory ~~free of~~ solvent vapors. There must be no solvents brought into the lab other than those used for extracting samples for volatiles or dissolving volatile standards (i.e. methanol, etc.). It is highly recommended that GC and GC/MS analysis for pesticides and semivolatiles be performed in a different room to avoid high background levels of methylene chloride and hexane.

7.4.3.1.7 Heat the sample to 40°C ± 1°C and purge the sample for 11.0 ± 0.1 minutes. Be sure the trap is cooler than 25°C.

7.4.3.1.8 Proceed with the analysis as outlined in Steps 7.4.1.12-7.4.1.17. Use 5 mL of the same water as in the blank. If saturated peaks occurred or would occur if a 1 g sample were analyzed, the medium-level method must be followed.

7.4.3.1.9 For low-level sediment/soils, add 10 uL of the matrix spike solution (Step 5.7) to the 5 mL of water (Step 7.4.3.1.3). The concentration for a 5 g sample would be equivalent to 50 ug/kg of each matrix spike standard.

7.4.3.2 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 tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of > 1.0 mg/kg should be analyzed by this method.

7.4.3.2.1 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 7.4.3.1.5. 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.)

7.4.3.2.2 Quickly add 9.0 mL of appropriate solvent. Cap and shake for 2 minutes.

that has stringent control of

NOTE: Steps 7.4.3.2.1 and 7.4.3.2.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory ~~free from~~ solvent vapors. There must be no solvents brought into the lab other than those used for extracting samples for volatiles or dissolving volatile standards (i.e. methanol, etc.). It is highly recommended that GC and GC/MS analysis for pesticides and semivolatiles be performed in a different room to avoid high background levels of methylene chloride and hexane.

7.4.3.2.3 Pipet approximately 1 mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. 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. The addition of a 100 uL aliquot of each of these extracts in Step 7.4.3.2.6 will give a concentration equivalent to 6,200 ug/kg of each surrogate standard.

7.4.3.2.4 The GC/MS system should be set up as in Steps 7.4.1.3-7.4.1.4. This should be done prior to the addition of the solvent extract to water.

7.4.3.2.5 The following information 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 (Method 3810 or 3820), 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 medium-level sample, start with 100 uL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SAMPLES

Approximate Concentration Range	Volume of 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.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 uL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 uL for analysis.

7.4.3.2.6 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 uL of internal standard solution; then add 10 uL of the surrogate spiking solution. Also add the volume of solvent extract determined in Step 7.4.3.2.5 and a volume of extraction or dissolution solvent to total 100 uL (excluding solvent in standards).

7.4.3.2.7 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.

7.4.3.2.8 Proceed with the analysis as outlined in Steps 7.4.1.12-7.4.1.17. Analyze all blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100 uL of the dilution solvent to simulate the sample conditions.

7.4.3.2.9 For a matrix spike in the medium-level sediment/soil samples, add 8.0 mL of methanol, 1.0 mL of surrogate spike solution (Step 5.9), and 1.0 mL of matrix spike solution (Step 5.13) as in Step 7.4.3.2.2. This results in a 6,200 ug/kg concentration of each matrix spike standard when added to a 4 g sample. Add a 100 uL aliquot of this extract to 5 mL of water for purging (as per Step 7.4.3.2.6).

7.5 Data interpretation

7.5.1 Qualitative analysis

7.5.1.1 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 analytical 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.

7.5.1.1.1 The intensities of the characteristic ions of a compound maximize in the same 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 chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.5.1.1.2 The RRT of the sample component is within 0.06 RRT units of the RRT of the standard component.

7.5.1.1.3 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%.)

7.5.1.1.4 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.

7.5.1.1.5 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.

7.5.1.2 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.

7.5.2 Quantitative analysis

7.5.2.1 When a compound has been identified, the quantification of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantification will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g. see Table 6).

7.5.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water and Water-Miscible Waste

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Step 7.2.6).

V_o = Volume of water purged (mL), taking into consideration any dilutions made.

Sediment/Soil, Sludge, and Waste

High-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)}$$

Low-level:

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)}{(A_{is})(RF)(W_s)}$$

where:

A_x, I_s, A_{is}, RF = Same as in water and water-miscble waste above.

V_t = Volume of total extract (uL) (use 10,000 uL or a factor of this when dilutions are made).

V_i = Volume of extract added (uL) for purging.

W_s = Weight of sample extracted or purged (g). The wet weight or dry weight may be used, depending upon the specific applications of the data.

7.5.2.3 Sediment/soil samples are generally reported on a dry weight basis, while sludges and wastes are reported on a wet weight basis. The % moisture of the sample (as calculated in Step 7.4.3.1.5) should be reported along with the data in either instance.

7.5.2.4 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.5.2.5 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all 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 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 calibration 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 blank should be processed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.3 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard 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 useable, 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.

8.4 Required instrument QC

8.4.1 The GC/MS system must be tuned to meet the BFB specifications in Step 7.2.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in Step 7.2.

8.4.3 The GC/MS system must meet the SPCC criteria specified in Step 7.3.3 and the CCC criteria in Step 7.3.4, each 12 hours.

8.5 To establish the ability to generate acceptable accuracy and precision on water samples, the analyst must perform the following operations.

8.5.1 A quality control (QC) reference sample concentrate is required containing each analyte at a concentration of 10 ug/mL in methanol. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

8.5.2 Prepare a QC reference sample to contain 20 ug/L of each analyte by adding 200 uL of QC reference sample concentrate to 100 mL of water. For the low level 25 mL a sample, spike at 5 ug/L.

8.5.3 Four 5 mL aliquots (or 25 mL for low level) of the well-mixed QC reference sample are analyzed according to the method beginning in Step 7.4.1.

8.5.4 Calculate the average percent recovery (R) and the standard deviation of the percent recovery (S_R), for the results. Ground water background corrections must be made before R and R_R calculation.

8.5.5 Tables 7 and 8 provide single laboratory recovery and precision data obtained for the method analytes from water. Similar results from dosed water should be expected by any experienced laboratory. Compare results obtained in Step 8.5.4 to the single laboratory recovery and precision data. If the results are not comparable, review potential problem areas and repeat the test. Results are comparable if the calculated percent relative standard deviation (RSD) does not exceed 2.6 times the single laboratory RSD or 20%, whichever is greater and the mean recovery lies within the interval R ± 3S or R ± 30%, which ever is greater.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Step 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes beginning with Step 8.5.2.

8.5.6.2 Beginning with Step 8.5.2, 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 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a blank and spiked replicates 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.

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

8.6.1.1 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 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in a water sample is not being checked against a specific limit, the spike should be at 20 ug/L (or 5 ug/L for low level) or 1 to 5 times higher than the background concentration determined in Step 8.6.2, whichever concentration would be larger. For other matrices, the recommended spiking concentration is 10 times the PQL.

8.6.2 Analyze one 5 mL sample aliquot (or 25 mL for low level) to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Step 8.5.1) appropriate for the background concentration in the sample. Spike a second 5 mL (or 25 mL for low level) 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.

8.6.2.1 Compare the percent recovery (R_j) for each analyte with QC acceptance criteria established from the analyses of laboratory control standards (Step 8.5). Monitor all data from dosed samples. Analyte recoveries must fall within the established control limits.

8.6.2.2 If recovery is not within limits, the following procedures are required.

8.6.2.2.1 Check to be sure there are no errors in calculations, matrix spike solutions and internal standards. Also, check instrument performance.

8.6.2.2.2 Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.

8.6.2.2.3 If the checks in 8.6.2.2.1 reveal no errors, the recovery problem encountered with the dosed sample is judged to be matrix-related, non system-related. The result for that analyte in the unspiked sample is labeled suspect/matrix to inform the user that the results are suspect due to matrix effects.

8.7 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) as in Step 8.6, calculate the average percent recovery (p) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $p - 2s_p$ to $p + 2s_p$. If $p = 90\%$ and $s_p = 10\%$, for example, the accuracy interval is expressed as 70-110%. Update the accuracy assessment for each analyte on a regular basis (e.g. after each five to ten new accuracy measurements).

8.8 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

8.8.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.8.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (p) and standard deviation of the percent recovery (s_p) for each of the surrogates.

8.8.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

Upper Control Limit (UCL) = $\bar{p} + 3s_p$
Lower Control Limit (LCL) = $\bar{p} - 3s_p$

8.8.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 9. The limits given in Table 9 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Step 8.8.3 must fall within those given in Table 9 for these matrices.

8.8.5 If recovery is not within limits, the following procedures are 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."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to assess the precision of the environmental measurements. When doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as gas chromatography with a dissimilar column or a different ionization mode using a mass spectrometer must be used. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.11 In recognition of the rapid advances occurring in chromatography, the analyst is permitted to modify GC columns, GC conditions, or detectors to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Step 8.4.

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 actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 ug/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 7. Calculated MDLs are presented in Table 1.

9.3 The method was tested using water spiked at 0.1 to 0.5 ug/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 8. MDL values were also calculated from these data and are presented in Table 2.

10.0 REFERENCES

1. Methods for the Determination of Organic Compounds in Finished Drinking Water and Raw Source Water Method 524.2; U.S. Environmental Protection Agency. Office of Research Development. Environmental Monitoring and Support Laboratory: Cincinnati, OH 1986.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Bellar, T.A.; Lichtenberg, J.J. J. Amer. Water Works Assoc. 1974, 66(12), 739-744.

4. Bellar, T.A.; Lichtenberg, J.J. "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.

5. Budde, W.L.; Eichelberger, J.W. "Performance Tests for the Evaluation of Computerized Gas Chromatography/Mass Spectrometry Equipment and Laboratories"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Cincinnati, OH 45268, April 1980; EPA-600/4-79-020.

6. Eichelberger, J.W.; Harris, L.E.; Budde, W.L. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems"; Analytical Chemistry 1975, 47, 995-1000.

7. Olynyk, P.; Budde, W.L.; Eichelberger, J.W. "Method Detection Limit for Methods 624 and 625"; Unpublished report, October 1980.

8. Provost, L.P.; Elder R.S. "Interpretation of Percent Recovery Data"; American Laboratory 1983, 15, 58-63.

9. Non Cryogenic Temperatures Program and Chromatogram, Private Communications; Myron Stephenson and Frank Allen, EPA Region IV Laboratory, Athens, GA.

10. 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.

11. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

12. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON WIDE BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 1[a]	Column 2[b]	Column 3[c]	MDL[d] (ug/L)
Dichlorodifluoromethane	1.55	0.70	--	0.10
Chloromethane	1.63	0.73	2.07	0.13
Vinyl Chloride	1.71	0.79	2.12	0.17
Bromomethane	2.01	0.96	2.26	0.11
Chloroethane	2.09	1.02	2.31	0.10
Trichlorofluoromethane	2.27	1.19	2.42	0.08
1,1-Dichloroethane	2.89	1.57	3.08	0.12
Methylene chloride	3.60	2.06	3.32	0.03
trans-1,2-Dichloroethene	3.98	2.36	3.48	0.06
1,1-Dichloroethane	4.85	2.93	4.10	0.04
2,2-Dichloropropane	6.01	3.80	4.43	0.35
cis-1,2-Dichloroethene	6.19	3.90	4.42	0.12
Chloroform	6.40	4.80	4.58	0.03
Bromochloromethane	6.74	4.38	4.54	0.04
1,1,1-Trichloroethane	7.27	4.84	5.09	0.08
Carbon tetrachloride	7.61	5.26	5.18	0.21
1,1-Dichloropropene	7.68	5.29	5.18	0.10
Benzene	8.23	5.67	5.29	0.04
1,2-Dichloroethane	8.40	5.83	5.29	0.06
Trichloroethene	9.59	7.27	6.07	0.19
1,2-Dichloropropane	10.09	7.66	6.20	0.04
Bromodichloromethane	10.59	8.49	6.39	0.08
Dibromomethane	10.65	7.93	6.27	0.24
Toluene	12.43	10.00	7.36	0.11
1,1,2-Trichloroethane	13.41	11.05	8.07	0.10
Tetrachloroethene	13.74	11.15	8.21	0.14
1,3-Dichloropropane	14.04	11.31	8.20	0.04
Dibromochloromethane	14.39	11.85	8.39	0.05
1,2-Dibromoethane	14.73	11.83	--	0.06
1-Chlorohexane	15.46	13.29	--	0.05
Chlorobenzene	15.76	13.01	9.33	0.04
1,1,1,2-Tetrachloroethane	15.94	13.33	9.41	0.05
Ethylbenzene	15.99	13.39	9.44	0.06
p-Xylene	16.12	13.69	9.56	0.13
m-Xylene	16.17	13.68	9.56	0.05
o-Xylene	17.11	14.52	10.32	0.11
Styrene	17.31	14.60	10.33	0.04
Bromoform	17.93	14.88	10.48	0.12
Isopropylbenzene	18.06	15.46	--	0.15
1,1,2,2-Tetrachloroethane	18.72	16.35	11.38	0.04
Bromobenzene	18.95	15.86	11.35	0.03

TABLE 1.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 1[a]	Column 2[b]	Column 3[c]	MDL[d] (ug/L)
1,2,3-Trichloropropane	19.02	16.23	11.40	0.32
n-Propylbenzene	19.06	16.41	--	0.04
2-Chlorotoluene	19.34	16.42	11.57	0.04
1,3,5-Trimethylbenzene	19.47	16.90	--	0.05
4-Chlorotoluene	19.50	16.72	12.08	0.06
tert-Butylbenzene	20.28	17.57	--	0.14
1,2,4-Trimethylbenzene	20.34	17.70	--	0.13
sec-Butylbenzene	20.79	18.09	--	0.13
p-Isopropyltoluene	21.20	18.52	--	0.12
1,3-Dichlorobenzene	21.22	18.14	13.16	0.12
1,4-Dichlorobenzene	21.55	18.39	13.27	0.03
n-Butylbenzene	22.22	19.49	--	0.11
1,2-Dichlorobenzene	22.52	19.17	14.10	0.03
1,2-Dibromo-3-chloropropane	24.53	21.08	--	0.26
1,2,4-Trichlorobenzene	26.55	23.08	--	0.04
Hexachlorobutadiene	26.99	23.68	--	0.11
Naphthalene	27.17	23.52	--	0.04
1,2,3-Trichlorobenzene	27.78	24.18	--	0.03
INTERNAL STANDARDS/SURROGATES				
4-Bromofluorobenzene	18.63	15.71	11.22	

[a]Column 1 - 60 m x 0.75 mm i.d. VOCOL capillary. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[b]Column 2 - 30 m x 0.53 mm i.d. DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°/min.

[c]Column 3 - 30 m x 0.53 mm i.d. DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 45°C for 2 minutes, then program to 200°C at 8°/min and hold for 6 minutes.

[d]MDL based on a 25 mL sample volume.

TABLE 2.
CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL)
FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (ug/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.06
Chloroethane	1.45	0.02
Trichlorofluoromethane	1.77	0.07
1,1-Dichloroethene	2.33	0.05
Methylene chloride	2.66	0.09
trans-1,2-Dichloroethene	3.54	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10

TABLE 2.
(Continued)

ANALYTE	RETENTION TIME (minutes) Column 3[a]	MDL[b] (ug/L)
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a]Column 3 - 30 m x 0.32 mm i.d. DB-5 capillary with um film thickness.

[b]MDL based on a 25 mL sample volume.

TABLE 3.
PRACTICAL QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

	Practical Quantitation Limits		
	Ground water		Low Soil/Sediment[b]
	ug/L		ug/kg
Volume of water purged	5 mL	25 mL	
All analytes in Table 1	5	1	5

[a]Practical Quantitation Limit (PQL) - The lowest level that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The PQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the PQL analyte level is selected for the lowest non-zero standard in the calibration curve. Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable. See the following information for further guidance on matrix-dependent PQLs.

[b]PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis; therefore, PQLs will be higher, based on the % moisture in each sample.

Other Matrices:	Factor[c]
Water miscible liquid waste	50
High-level soil and sludges	125
Non-water miscible waste	500

[c]PQL = [PQL for low soil sediment (Table 3)] X [Factor]. For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4.
BFB MASS - INTENSITY SPECIFICATIONS (4-BROMOFLUOROBENZENE)

Mass	Intensity Required (relative abundance)
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 5.
CHARACTERISTIC MASSES (M/Z) FOR PURGEABLE ORGANIC COMPOUNDS

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Benzene	78	-
Bromobenzene	156	77,158
Bromochloromethane	128	49,130
Bromodichloromethane	83	85,127
Bromoform	173	175,254
Bromomethane	94	96
n-Butylbenzene	91	92,134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91,134
Carbon tetrachloride	117	119
Chlorobenzene	112	77,114
Chloroethane	64	66
Chloroform	83	85
Chloromethane	50	52
2-Chlorotoluene	126	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155,157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109,188
Dibromomethane	93	95,174
1,2-Dichlorobenzene	146	111,148
1,3-Dichlorobenzene	146	111,148
1,4-Dichlorobenzene	146	111,148
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65,83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61,63
cis-1,2-Dichloroethene	96	61,98
trans-1,2-Dichloroethene	96	61,98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,1-Dichloropropene	75	110,77
Ethylbenzene	91	106
Hexachlorobutadiene	225	223,227
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134,91
Methylene chloride	84	86,49
Naphthalene	128	-
n-Propylbenzene	120	120
Styrene	104	78
1,1,1,2-Tetrachloroethane	131	133,119

TABLE 5.
(Continued)

Analyte	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,1,1,2-Tetrachloroethane	83	131,85
Tetrachloroethene	166	168,129
Toluene	92	91
1,2,3-Trichlorobenzene	180	182,145
1,2,4-Trichlorobenzene	180	182,145
1,1,1-Trichloroethane	97	99,61
1,1,2-Trichloroethane	83	97,85
Trichloroethene	95	130,132
Trichlorofluoromethane	101	103
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
INTERNAL STANDARDS/SURROGATES		
4-Bromofluorobenzene	95	174,176
Dibromofluoromethane	113	
Toluene-d_8	98	
Pentafluorobenzene	168	
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	

TABLE 6.
VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES
ASSIGNED FOR QUANTITATION

Pentafluorobenzene	1,4-Difluorobenzene
Acetone	Benzene
Acrolein	Bromodichloromethane
Acrylonitrile	Bromofluorobenzene (surrogate)
Bromochloromethane	Carbon tetrachloride
Bromomethane	2-Chloroethyl vinyl ether
2-Butanone	1,2-Dibromoethane
Carbon disulfide	Dibromomethane
Chloroethane	1,2-Dichloroethane
Chloroform	1,2-Dichloroethane-d_4 (surrogate)
Chloromethane	1,2-Dichloropropane
Dichlorodifluoromethane	1,1-Dichloropropene
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,1-Dichloroethene	trans-1,3-Dichloropropene
cis-1,2-Dichloroethene	4-Methyl-2-pentanone
trans-1,2-Dichloroethene	Toluene
2,2-Dichloropropane	Toluene-d_8 (surrogate)
Iodomethane	1,1,2-Trichloroethane
Methylene chloride	Trichloroethene
1,1,1-Trichloroethane	
Trichlorofluoromethane	1,4-Dichlorobenzene-d_4
Vinyl acetate	
Vinyl chloride	Bromobenzene
	n-Butylbenzene
Chlorobenzene-d_5	sec-Butylbenzene
	tert-Butylbenzene
Bromoform	2-Chlorotoluene
Chlorodibromomethane	4-Chlorotoluene
Chlorobenzene	1,2-Dibromo-3-chloropropane
1,3-Dichloropropane	1,2-Dichlorobenzene
Ethylbenzene	1,3-Dichlorobenzene
2-Hexanone	1,4-Dichlorobenzene
Styrene	Hexachlorobutadiene
1,1,1,2-Tetrachloroethane	Isopropyl benzene
Tetrachloroethene	p-Isopropyltoluene
Xylene	Naphthalene
	n-Propylbenzene
	1,1,2,2-Tetrachloroethane
	1,2,3-Trichlorobenzene
	1,2,4-Trichlorobenzene
	1,2,3-Trichloropropane
	1,2,4-Trimethylbenzene
	1,3,5-Trimethylbenzene

TABLE 7.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN

Analyte	Conc. Range, ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7

TABLE 7.
(Continued)

Analyte	Conc. Range, ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Methylene chloride	0.1 - 10	30	95	5.0	5.3
Naphthalene	0.1 -100	31	104	8.6	8.2
n-Propylbenzene	0.1 - 10	31	100	5.8	5.8
Styrene	0.1 -100	39	102	7.3	7.2
1,1,1,2-Tetrachloroethane	0.5 - 10	24	90	6.1	6.8
1,1,2,2-Tetrachloroethane	0.1 - 10	30	91	5.7	6.3
Tetrachloroethene	0.5 - 10	24	89	6.0	6.8
Toluene	0.5 - 10	18	102	8.1	8.0
1,2,3-Trichlorobenzene	0.5 - 10	18	109	9.4	8.6
1,2,4-Trichlorobenzene	0.5 - 10	18	108	9.0	8.3
1,1,1-Trichloroethane	0.5 - 10	18	98	7.9	8.1
1,1,2-Trichloroethane	0.5 - 10	18	104	7.6	7.3
Trichloroethene	0.5 - 10	24	90	6.5	7.3
Trichlorofluoromethane	0.5 - 10	24	89	7.2	8.1
1,2,3-Trichloropropane	0.5 - 10	16	108	15.6	14.4
1,2,4-Trimethylbenzene	0.5 - 10	18	99	8.0	8.1
1,3,5-Trimethylbenzene	0.5 - 10	23	92	6.8	7.4
Vinyl chloride	0.5 - 10	18	98	6.5	6.7
o-Xylene	0.1 - 31	18	103	7.4	7.2
m-Xylene	0.1 - 10	31	97	6.3	6.5
p-Xylene	0.5 - 10	18	104	8.0	7.7

[a]Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

[b]Standard deviation was calculated by pooling data form three levels.

TABLE 8.
SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR
VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED
WITH A NARROW BORE CAPILLARY COLUMN

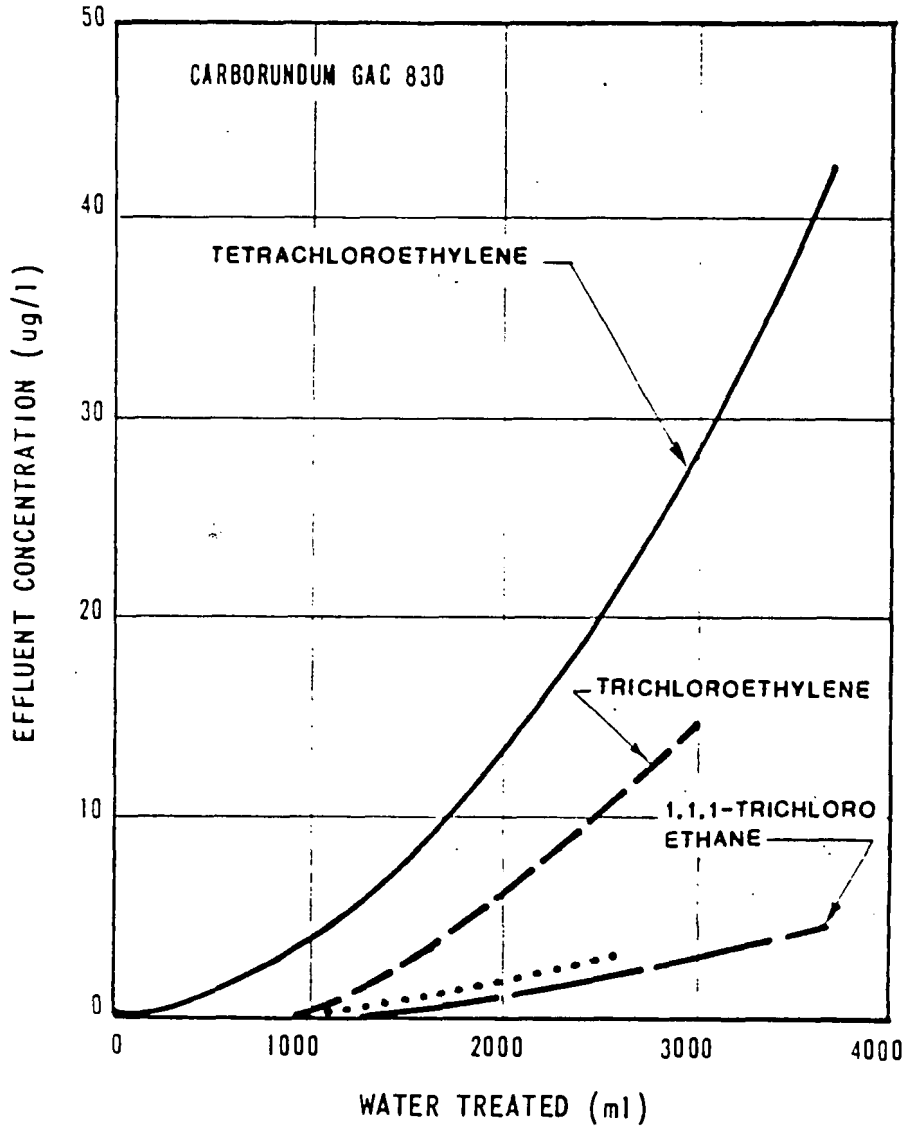
Analyte	Conc. ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.7	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5

TABLE 8.
(Continued)

Analyte	Conc. ug/L	Number of Samples	Recovery,[a] %	Standard Deviation of Recovery[b]	Percent Rel. Std. Dev.
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
o-Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a]Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

MINI-COLUMN TEST RESULTS



Define:

- Controlling VOC

- Carbon Usage based on:

$$\text{Carbon usage (lbs/1,000 gal)} = \frac{W}{V} \times 8461.5$$

where W = weight of carbon (0.1 gm)
V = volume treated (ml)

- Preliminary Process Design

41

TABLE 9.
SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117

[a]Single laboratory data for guidance only.

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS: CAPILLARY COLUMN TECHNIQUE

1.0 SCOPE AND APPLICATION

1.1 Method 8270 is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. Direct injection of a sample may be used in limited applications.

1.2 Method 8270 can be used to quantify most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols. See Table 1 for a list of compounds and their characteristic ions that have been evaluated on the specified GC/MS system.

1.3 The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal decomposition in the inlet of the gas chromatograph, chemical reaction in acetone solution, and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

1.4 The practical quantitation limit (PQL) of Method 8270 for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 ug/L for ground water samples (see Table 2). PQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method.

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Acenaphthene	15.13	154	153, 152
Acenaphthene-d_{10} (I.S.)	15.05	164	162, 160
Acenaphthylene	14.57	152	151, 153
Acetophenone	7.96[a]	105	77, 51
Aldrin	--	66	263, 220
Aniline	5.68	93	66, 65
Anthracene	19.77	178	176, 179
4-Aminobiphenyl	19.18[a]	169	168, 170
Aroclor-1016	--	222	260, 292
Aroclor-1221	--	190	224, 260
Aroclor-1232	--	190	224, 260
Aroclor-1242	--	222	256, 292
Aroclor-1248	--	292	362, 326
Aroclor-1254	--	292	362, 326
Aroclor-1260	--	360	362, 394
Benzidine	23.87	184	92, 185
Benzoic acid	9.38	122	105, 77
Benzo(a)anthracene	27.83	228	229, 226
Benzo(b)fluoranthene	31.45	252	253, 125
Benzo(k)fluoranthene	31.55	252	253, 125
Benzo(g,h,i)perylene	41.43	276	138, 277
Benzo(a)pyrene	32.80	252	253, 125
Benzyl alcohol	6.78	108	79, 77
α-BHC	--	183	181, 109
β-BHC	--	181	183, 109
δ-BHC	--	183	181, 109
γ-BHC (Lindane)	--	183	181, 109
Bis(2-chloroethoxy)methane	9.23	93	95, 123
Bis(2-chloroethyl)ether	5.82	93	63, 95
Bis(2-chloroisopropyl)ether	7.22	45	77, 121
Bis(2-ethylhexyl)phthalate	28.47	149	167, 279
4-Bromophenyl phenyl ether	18.27	248	250, 141
Butyl benzyl phthalate	26.43	149	91, 206
Chlordane	--	373	375, 377
4-Chloroaniline	10.08	127	129
1-Chloronaphthalene	13.65[a]	162	127, 164
2-Chloronaphthalene	13.30	162	127, 164
4-Chloro-3-methylphenol	11.68	107	144, 142
2-Chlorophenol	5.97	128	64, 130
4-Chlorophenyl phenyl ether	16.78	204	206, 141
Chrysene	27.97	228	226, 229
Chrysene-d_{12} (I.S.)	27.88	240	120, 236
4,4'-DDD	--	235	237, 165
4,4'-DDE	--	246	248, 176

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
4,4'-DDT	--	235	237, 165
Dibenz(a,j)acridine	32.55[a]	279	280, 277
Dibenz(a,h)anthracene	39.82	278	139, 279
Dibenzofuran	15.63	168	139
Di-n-butylphthalate	21.78	149	150, 104
1,3-Dichlorobenzene	6.27	146	148, 111
1,4-Dichlorobenzene	6.40	146	148, 111
1,4-Dichlorobenzene-d_4 (I.S.)	6.35	152	150, 115
1,2-Dichlorobenzene	6.85	146	148, 111
3,3'-Dichlorobenzidine	27.88	252	254, 126
2,4-Dichlorophenol	9.48	162	164, 98
2,6-Dichlorophenol	10.05[a]	162	164, 98
Dieldrin	--	79	263, 279
Diethylphthalate	16.70	149	177, 150
p-Dimethylaminoazobenzene	24.48[a]	120	225, 77
7,12-Dimethylbenz(a)anthracene	29.54[a]	256	241, 257
α-,α-Dimethylphenethylamine	9.51[a]	58	91, 42
2,4-Dimethylphenol	9.03	122	107, 121
Dimethylphthalate	14.48	163	194, 164
4,6-Dinitro-2-methylphenol	17.05	198	51, 105
2,4-Dinitrophenol	15.35	184	63, 154
2,4-Dinitrotoluene	15.80	165	63, 89
2,6-Dinitrotoluene	14.62	165	63, 89
Diphenylamine	17.54[a]	169	168, 167
1,2-Diphenylhydrazine	--	77	105, 182
Di-n-octylphthalate	30.48	149	167, 43
Endosulfan I	--	195	339, 341
Endosulfan II	--	337	339, 341
Endosulfan sulfate	--	272	387, 422
Endrin	--	263	82, 81
Endrin aldehyde	--	67	345, 250
Endrin ketone	--	317	67, 319
Ethyl methanesulfonate	5.33[a]	79	109, 97
Fluoranthene	23.33	202	101, 203
Fluorene	16.70	166	165, 167
2-Fluorobiphenyl (surr.)	--	172	171
2-Fluorophenol (surr.)	--	112	64
Heptachlor	--	100	272, 274
Heptachlor epoxide	--	353	355, 351
Hexachlorobenzene	18.65	284	142, 249
Hexachlorobutadiene	10.43	225	223, 227
Hexachlorocyclopentadiene	12.60	237	235, 272
Hexachloroethane	7.65	117	201, 199
Indeno(1,2,3-cd)pyrene	39.52	276	138, 227

TABLE 1. CHARACTERISTIC IONS FOR SEMIVOLATILE COMPOUNDS (Continued)

Compound	Retention Time (min)	Primary Ion	Secondary Ion(s)
Isophorone	8.53	82	95, 138
Methoxychlor	--	227	228
3-Methylcholanthrene	31.14[a]	268	253, 267
Methyl methanesulfonate	4.32[a]	80	79, 65
2-Methylnaphthalene	11.87	142	141
2-Methylphenol (o-cresol)	7.22	108	107, 79
4-Methylphenol (p-cresol)	7.60	108	107, 79
Naphthalene	9.82	128	129, 127
Naphthalene-d_8 (I.S.)	9.75	136	68
1-Naphthylamine	15.80[a]	143	115, 116
2-Naphthylamine	16.00[a]	143	115, 116
2-Nitroaniline	13.75	65	92, 138
3-Nitroaniline	15.02	138	108, 92
4-Nitroaniline	16.90	138	108, 92
Nitrobenzene	7.87	77	123, 65
Nitrobenzene-d_5 (surr.)	--	82	128, 54
2-Nitrophenol	8.75	139	109, 65
4-Nitrophenol	15.80	139	109, 65
N-Nitroso-di-n-butylamine	10.99[a]	84	57, 41
N-Nitrosodimethylamine	--	42	74, 44
N-Nitrosodiphenylamine	17.17	169	168, 167
N-Nitrosodipropylamine	7.55	70	42, 101, 130
N-Nitrosopiperidine	--	42	114, 55
Pentachlorobenzene	15.64[a]	250	252, 248
Pentachloronitrobenzene	19.47[a]	295	237, 142
Pentachlorophenol	19.25	266	264, 268
Perylene-d_{12} (I.S.)	33.05	264	260, 265
Phenacetin	18.59[a]	108	109, 179
Phenanthrene	19.62	178	179, 176
Phenanthrene-d_{10} (I.S.)	19.55	188	94, 80
Phenol	5.77	94	65, 66
Phenol-d_6 (surr.)	--	99	42, 71
2-Picoline	3.75[a]	93	66, 92
Pronamide	19.61[a]	173	175, 145
Pyrene	24.02	202	200, 203
Terphenyl-d_{14} (surr.)	--	244	122, 212
1,2,4,5-Tetrachlorobenzene	13.62[a]	216	214, 218
2,3,4,6-Tetrachlorophenol	16.09[a]	232	230, 131
2,4,6-Tribromophenol (surr.)	--	330	332, 141
1,2,4-Trichlorobenzene	9.67	180	182, 145
2,4,5-Trichlorophenol	13.00	196	198, 200
2,4,6-Trichlorophenol	12.85	196	198, 200
Toxaphene	--	159	231, 233

I.S. = internal standard
surr. = surrogate

[a]Estimated retention times.

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS**

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Phenol	108-95-2	10	660
bis(2-Chloroethyl) ether	111-44-4	10	660
2-Chlorophenol	95-57-8	10	660
1,3-Dichlorobenzene	541-73-1	10	660
1,4-Dichlorobenzene	106-46-7	10	660
Benzyl Alcohol	100-51-6	20	1300
1,2-Dichlorobenzene	95-50-1	10	660
2-Methylphenol	95-48-7	10	660
bis(2-Chloroisopropyl) ether	39638-32-9	10	660
4-Methylphenol	106-44-5	10	660
N-Nitroso-Di-N-propylamine	621-64-7	10	660
Hexachloroethane	67-72-1	10	660
Nitrobenzene	98-95-3	10	660
Isophorone	78-59-1	10	660
2-Nitrophenol	88-75-5	10	660
2,4-Dimethylphenol	105-67-9	10	660
Benzoic Acid	65-85-0	50	3300
bis(2-Chloroethoxy) methane	111-91-1	10	660
2,4-Dichlorophenol	120-83-2	10	660
1,2,4-Trichlorobenzene	120-82-1	10	660
Naphthalene	91-20-3	10	660
4-Chloroaniline	106-47-8	20	1300
Hexachlorobutadiene	87-68-3	10	660
4-Chloro-3-methylphenol	59-50-7	20	1300
2-Methylnaphthalene	91-57-6	10	660
Hexachlorocyclopentadiene	77-47-4	10	660
2,4,6-Trichlorophenol	88-06-2	10	660
2,4,5-Trichlorophenol	95-95-4	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semivolatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
2-Chloronaphthalene	91-58-7	10	660
2-Nitroaniline	88-74-4	50	3300
Dimethyl phthalate	131-11-3	10	660
Acenaphthylene	208-96-8	10	660
3-Nitroaniline	99-09-2	50	3300
Acenaphthene	83-32-9	10	660
2,4-Dinitrophenol	51-28-5	50	3300
4-Nitrophenol	100-02-7	50	3300
Dibenzofuran	132-64-9	10	660
2,4-Dinitrotoluene	121-14-2	10	660
2,6-Dinitrotoluene	606-20-2	10	660
Diethylphthalate	84-66-2	10	660
4-Chlorophenyl phenyl ether	7005-72-3	10	660
Fluorene	86-73-7	10	660
4-Nitroaniline	100-01-6	50	3300
4,6-Dinitro-2-methylphenol	534-52-1	50	3300
N-Nitrosodiphenylamine	86-30-6	10	660
4-Bromophenyl phenyl ether	101-55-3	10	660
Hexachlorobenzene	118-74-1	10	660
Pentachlorophenol	87-86-5	50	3300
Phenanthrene	85-01-8	10	660
Anthracene	120-12-7	10	660
Di-n-butylphthalate	84-74-2	10	660
Fluoranthene	206-44-0	10	660
Pyrene	129-00-0	10	660
Butyl benzyl phthalate	85-68-7	10	660
3,3'-Dichlorobenzidine	91-94-1	20	1300
Benzo(a)anthracene	56-55-3	10	660
bis(2-ethylhexyl)phthalate	117-81-7	10	660

TABLE 2. PRACTICAL QUANTITATION LIMITS (PQL) FOR SEMIVOLATILE ORGANICS** (Continued)

Semi-Volatiles	CAS Number	Practical Quantitation Limits*	
		Ground Water	Low Soil/Sediment[1]
		ug/L	ug/Kg
Chrysene	218-01-9	10	660
Di-n-octyl phthalate	117-84-0	10	660
Benzo(b)fluoranthene	205-99-2	10	660
Benzo(k)fluoranthene	207-08-9	10	660
Benzo(a)pyrene	50-32-8	10	660
Indeno(1,2,3-cd)pyrene	193-39-5	10	660
Dibenz(a,h)anthracene	53-70-3	10	660
Benzo(g,h,i)perylene	191-24-2	10	660

*PQLs listed for soil/sediment are based on wet weight. Normally data is reported on a dry weight basis, therefore, PQLs will be higher based on the % moisture in each sample. This is based on a 30-g sample and gel permeation chromatography cleanup.

**Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achieveable.

Other Matrices	Factor[1]
Medium-level soil and sludges by sonicator	7.5
Non-water-miscible waste	75

[1]PQL = [PQL for Ground Water (Table 2)] X [Factor].

2.0 SUMMARY OF METHOD

2.1 Prior to using this method, the samples should be prepared for chromatography using the appropriate sample preparation and cleanup methods. This method describes chromatographic conditions that will allow for the separation of the compounds in the extract.

3.0 INTERFERENCES

3.1 Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Determine if the source of interference is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

3.2 Contamination by carryover can occur whenever high-level and low-level 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/mass spectrometer system:

4.1.1 **Gas chromatograph:** An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection and all required accessories, including syringes, analytical columns, and gases. The capillary column should be directly coupled to the source.

4.1.2 **Column:** 30-m x 0.25-mm I.D. (or 0.32-mm I.D.) 1-um film thickness silicon-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

4.1.3 **Mass spectrometer:** Capable of scanning from 35 to 500 amu every 1 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for decafluorotriphenylphosphine (DFTPP) which meets all of the criteria in Table 3 when 1 uL of the GC/MS tuning standard is injected through the GC (50 ng of DFTPP).

4.1.4 **GC/MS interface:** Any GC-to-MS interface that gives acceptable calibration points at 50 ng per injection for each compound of interest and achieves acceptable tuning performance criteria may be used.

4.1.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program. The computer must have

TABLE 3. DFTPP KEY IONS AND ION ABUNDANCE CRITERIA[a]

Mass	Ion Abundance Criteria
51	30-60% of mass 198
68	<2% of mass 69
70	<2% of mass 69
127	40-60% of mass 198
197	<1% of mass 198
198	Base peak, 100% relative abundance
199	5-9% of mass 198
275	10-30% of mass 198
365	>1% of mass 198
441	Present but less than mass 443
442	>40% of mass 198
443	17-23% of mass 442

[a]J.W. Eichelberger, L.E. Harris, and W.L. Budde. "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry", Analytical Chemistry, 47, 995 (1975).

software that can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library should also be available.

4.2 Syringe: 10-uL.

5.0 REAGENTS

5.1 Stock standard solutions (1.00 ug/uL): Standard solutions can be prepared from pure standard materials or purchased as certified solutions.

5.1.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in pesticide quality acetone or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.1.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.1.3 Stock standard solutions must be replaced after 1 yr or sooner if comparison with quality control check samples indicates a problem.

5.2 Internal standard solutions: The internal standards recommended are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. Other compounds may be used as internal standards as long as the requirements given in Paragraph 7.3.2 are met. Dissolve 200 mg of each compound with a small volume of carbon disulfide. Transfer to a 50-mL volumetric flask and dilute to volume with methylene chloride so that the final solvent is approximately 20% carbon disulfide. Most of the compounds are also soluble in small volumes of methanol, acetone, or toluene, except for perylene-d_{12}. The resulting solution will contain each standard at a concentration of 4,000 ng/uL. Each 1-mL sample extract undergoing analysis should be spiked with 10 uL of the internal standard solution, resulting in a concentration of 40 ng/uL of each internal standard. Store at 4°C or less when not being used.

5.3 GC/MS tuning standard: A methylene chloride solution containing 50 ng/uL of decafluorotriphenylphosphine (DFTPP) should be prepared. The

standard should also contain 50 ng/uL each of 4,4'-DDT, pentachlorophenol, and benzidine to verify injection port inertness and GC column performance. Store at 4°C or less when not being used.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared. One of the calibration standards should be at a concentration near, but above, the method detection limit; the others should correspond to the range of concentrations found in real samples but should not exceed the working range of the GC/MS system. 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). Each 1-mL aliquot of calibration standard should be spiked with 10 uL of the internal standard solution prior to analysis. All standards should be stored at -10°C to -20°C and should be freshly prepared once a year, or sooner if check standards indicate a problem. The daily calibration standard should be prepared weekly and stored at 4°C.

5.5 Surrogate standards: The recommended surrogate standards are phenol-d_6, 2-fluorophenol, 2,4,6-tribromophenol, nitrobenzene-d_5, 2-fluorobiphenyl, and p-terphenyl-d_{14}. See Method 3500 for the instructions on preparing the surrogate standards. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

5.6 Matrix spike standards: See Method 3500 for instructions on preparing the matrix spike standard. Determine what concentration should be in the blank extracts after all extraction, cleanup, and concentration steps. Inject this concentration into the GC/MS to determine recovery of surrogate standards in all blanks, spikes, and sample extracts. Take into account all dilutions of sample extracts.

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 preparation: Samples must be prepared by one of the following methods prior to GC/MS analysis.

Matrix	Methods
Water	3510, 3520
Soil/sediment	3540, 3550
Waste	3540, 3550, 3580

7.1.1 **Direct injection:** In very limited applications direct injection of the sample into the GC/MS system with a 10 uL syringe may be appropriate. The detection limit is very high (approximately 10,000 ug/L); therefore, it is only permitted where concentrations in excess of 10,000 ug/L are expected. The system must be calibrated by direct injection.

7.2 Extract cleanup: Extracts may be cleaned up by any of the following methods prior to GC/MS analysis.

Compounds	Methods
Phenols	3630, 3640, 8040[a]
Phthalate esters	3610, 3620, 3640
Nitrosamines	3610, 3620, 3640
Organochlorine pesticides & PCBs	3620, 3640, 3660
Nitroaromatics and cyclic ketones	3620, 3640
Polynuclear aromatic hydrocarbons	3611, 3630, 3640
Haloethers	3620, 3640
Chlorinated hydrocarbons	3620, 3640
Organophosphorous pesticides	3620, 3640
Petroleum waste	3611, 3650
All priority pollutant base, neutral, and acids	3640

[a]Method 8040 includes a derivatization technique followed by GC/ECD analysis, if interferences are encountered on GC/FID.

7.3 Initial calibration: The recommended GC/MS operating conditions:

Mass range: 35-500 amu
Scan time: 1 sec/scan
Initial column temperature and hold time: 40°C for 4 min
Column temperature program: 40-270°C at 10°C/min
Final column temperature hold: 270°C (until benzo[g,h,i]perylene has eluted)
Injector temperature: 250-300°C
Transfer line temperature: 250-300°C
Source temperature: According to manufacturer's specifications
Injector: Grob-type, splitless
Sample volume: 1-2 uL
Carrier gas: Hydrogen at 50 cm/sec or helium at 30 cm/sec.

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 3 for a 50-ng injection of DFTPP. Analyses should not begin until all these criteria are met. Background subtraction should be straightforward and designed only to eliminate column bleed or instrument background ions. The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. Degradation of DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at their normal responses, and no peak tailing should be visible. If degradation is excessive and/or poor chromatography is noted, the injection port may require cleaning. It may also be necessary to break off the first 6-12 in. of the capillary column.

7.3.2 The internal standards selected in Paragraph 5.1 should permit most of the components of interest in a chromatogram to have retention times of 0.80-1.20 relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion, i.e., for 1,4-dichlorobenzene-d_4 use m/z 152 for quantitation.

7.3.3 Analyze 1 uL of each calibration standard (containing internal standards) and tabulate the area of the primary characteristic ion against concentration for each compound (as indicated in Table 1). Figure 1 shows a chromatogram of a calibration standard containing base/neutral and acid analytes. Calculate response factors (RFs) for each compound 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_x = Concentration of the compound being measured (ng/uL).

C_{is} = Concentration of the specific internal standard (ng/uL).

7.3.4 The average RF should be calculated for each compound. The percent relative standard deviation (%RSD = 100[SD/$\overline{RF}$]) should also be calculated for each compound. The %RSD should be less than 30% for each compound. However, the %RSD for each individual Calibration Check Compound (CCC) (see Table 4) must be less than 30%. The relative retention times of each compound in each calibration run should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.5 A system performance check must be performed to ensure that minimum average RFs are met before the calibration curve is used. For semivolatiles, the System Performance Check Compounds (SPCCs) are: N-nitroso-di-n-propylamine; hexachlorocyclopentadiene; 2,4-dinitrophenol; and 4-nitrophenol. The minimum acceptable average $\overline{RF}$ for these compounds SPCCs is 0.050. These SPCCs typically have very low RFs (0.1-0.2) and tend to decrease in response as the chromatographic system begins to deteriorate or the standard material begins to deteriorate. They are usually the first to show poor performance. Therefore, they must meet the minimum requirement when the system is calibrated.

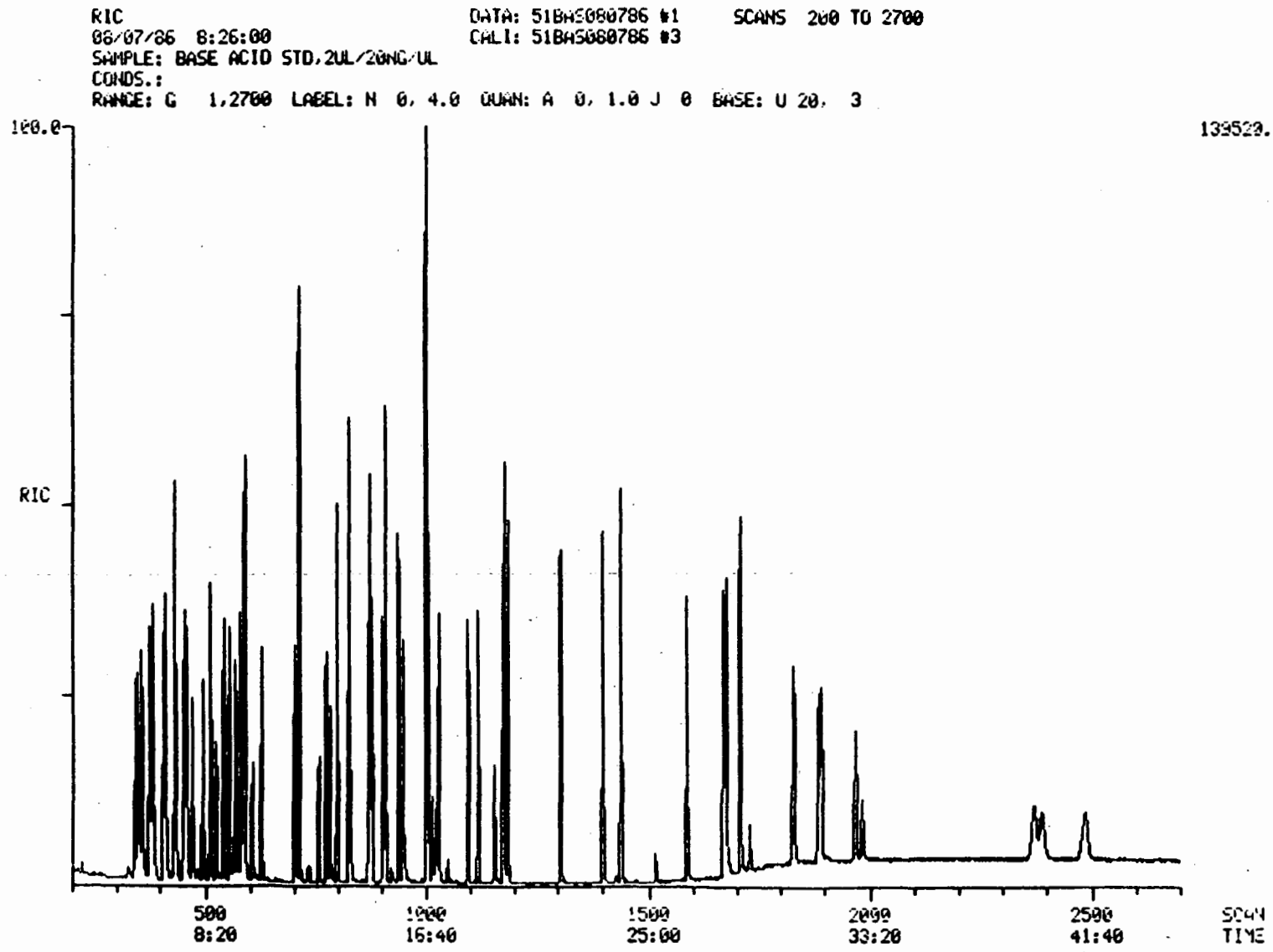


Figure 1. Gas chromatogram of base/neutral and acid calibration standard.

TABLE 4. CALIBRATION CHECK COMPOUNDS

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-n-phenylamine	Phenol
Di-n-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pyrene	

7.4 Daily GC/MS calibration:

7.4.1 Prior to analysis of samples, the GC/MS tuning standard must be analyzed. A 50-ng injection of DFTPP must result in a mass spectrum for DFTPP which meets the criteria given in Table 3. These criteria must be demonstrated during each 12-hr shift.

7.4.2 A calibration standard(s) at mid-level concentration containing all semivolatile analytes, including all required surrogates, must be performed every 12-hr during analysis. Compare the response factor data from the standards every 12-hr with the average response factor from the initial calibration for a specific instrument as per the SPCC (Paragraph 7.4.3) and CCC (Paragraph 7.4.4) criteria.

7.4.3 **System Performance Check Compounds** (SPCCs): A system performance check must be made during every 12 hr shift. 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 met, the system must be evaluated, and corrective action must be taken before sample analysis begins. The minimum RF for semivolatile SPCCs is 0.050. Some possible problems are standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before analysis begins.

7.4.4 **Calibration Check Compounds** (CCCs): After the system performance check is met, CCCs listed in Table 4 are used to check the validity of the initial calibration. Calculate the percent difference using:

$$\% \text{ Difference} = \frac{\overline{RF}_I - RF_C}{\overline{RF}_I} \times 100$$

where:

$\overline{RF}_I$ = average response factor from initial calibration.

RF_C = response factor from current verification check standard.

If the percent difference for any compound is greater than 20, the laboratory should consider this a warning limit. If the percent difference for each CCC is less than 30%, the initial calibration is assumed to be valid. If the criterion is not met (>30% difference) for any one CCC, corrective action MUST be taken. Problems similar to those listed under SPCCs could affect this criterion. If no source of the problem can be determined after corrective action has been taken, a new five-point calibration MUST be generated. This criterion MUST be met before sample analysis begins.

7.4.5 The internal standard responses and retention times in the calibration check standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 sec from the last check calibration (12 hr), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

7.5 GC/MS analysis:

7.5.1 It is highly recommended that the extract be screened on a GC/FID or GC/PID using the same type of capillary column. This will minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds.

7.5.2 Spike the 1-mL extract obtained from sample preparation with 10 uL of the internal standard solution just prior to analysis.

7.5.3 Analyze the 1-mL extract by GC/MS using a 30-m x 0.25-mm (or 0.32-mm) silicone-coated fused-silica capillary column. The volume to be injected should ideally contain 100 ng of base/neutral and 200 ng of acid surrogates (for a 1 uL injection). The recommended GC/MS operating conditions to be used are specified in Paragraph 7.3.

7.5.4 If the response for any quantitation ion exceeds the initial calibration curve range of the GC/MS system, extract dilution must take place. Additional internal standard must be added to the diluted extract to maintain the required 40 ng/uL of each internal standard in the extracted volume. The diluted extract must be reanalyzed.

7.5.5 Perform all qualitative and quantitative measurements as described in Paragraph 7.6. Store the extracts at 4°C, protected from light in screw-cap vials equipped with unpierced Teflon-lined septa.

7.6 Data interpretation:

7.6.1 **Qualitative analysis:**

7.6.1.1 An analyte (e.g., those listed in Table 1) is identified by comparison of the sample mass spectrum with the mass spectrum of a standard of the suspected compound (standard reference spectrum). Mass spectra for standard reference should be obtained on the user's GC/MS within the same 12 hours as the sample analysis. These standard reference spectra may be obtained through analysis of the calibration standards. Two criteria must be satisfied to verify identification: (1) elution of sample component at the same GC relative retention time (RRT) as the standard component; and (2) correspondence of the sample component and the standard component mass spectrum.

7.6.1.1.1 The sample component RRT must compare within ± 0.06 RRT units of the RRT of the standard component. For reference, the standard must be run within the same 12 hrs as the sample. If coelution of interfering components prohibits accurate assignment of the sample component RRT from the total ion chromatogram, the RRT should be assigned by using extracted ion current profiles for ions unique to the component of interest.

7.6.1.1.2 All ions present in the standard mass spectra at a relative intensity greater than 10% (most abundant ion in the spectrum equals 100% must be present in the sample spectrum.

7.6.1.1.3 The relative intensities of ions specified in Paragraph 7.6.1.1.2 must agree within plus or minus 20% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 30 and 70 percent.

7.6.1.2 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. 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 spectra with the nearest library searches will the mass spectral interpretation specialist assign a tentative identification. 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 ±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 sample the 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.

7.6.2 **Quantitative analysis:**

7.6.2.1 When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of that of a given analyte (e.g., see Table 5).

7.6.2.2 Calculate the concentration of each identified analyte in the sample as follows:

Water:

$$\text{concentration (ug/L)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_o)(V_i)}$$

where:

A_x = Area of characteristic ion for compound being measured.

I_s = Amount of internal standard injected (ng).

V_t = Volume of total extract, taking into account dilutions (i.e., a 1-to-10 dilution of a 1-mL extract will mean V_t = 10,000 uL. If half the base/neutral extract and half the acid extract are combined, V_t = 2,000.

A_{is} = Area of characteristic ion for the internal standard.

RF = Response factor for compound being measured (Paragraph 7.3.3).

V_o = Volume of water extracted (mL).

V_i = Volume of extract injected (uL).

Sediment/Soil Sludge (on a dry-weight basis) and Waste (normally on a wet-weight basis):

$$\text{concentration (ug/kg)} = \frac{(A_x)(I_s)(V_t)}{(A_{is})(RF)(V_i)(W_s)(D)}$$

where:

A_x, I_s, V_t, A_{is}, RF, V_i = same as for water.

W_s = weight of sample extracted or diluted in grams.

D = (100 - % moisture in sample)/100, or 1 for a wet-weight basis.

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION

1,4-Dichlorobenzene-d_4	Naphthalene-d_8	Acenaphthene-d_{10}
Aniline	Acetophenone	Acenaphthene
Benzyl alcohol	Benzoic acid	Acenaphthylene
Bis(2-chloroethyl)ether	Bis(2-chloroethoxy)methane	1-Chloronaphthalene
Bis(2-chloroisopropyl)ether	4-Chloroaniline	2-Chloronaphthalene
2-Chlorophenol	4-Chloro-3-methylphenol	4-Chlorophenyl phenyl ether
1,3-Dichlorobenzene	2,4-Dichlorophenol	Dibenzofuran
1,4-Dichlorobenzene	2,6-Dichlorophenol	Diethyl phthalate
1,2-Dichlorobenzene	α,α-Dimethyl-phenethylamine	Dimethyl phthalate
Ethyl methanesulfonate	2,4-Dimethylphenol	2,4-Dinitrophenol
2-Fluorophenol (surr.)	Hexachlorobutadiene	2,4-Dinitrotoluene
Hexachloroethane	Isophorone	2,6-Dinitrotoluene
Methyl methanesulfonate	2-Methylnaphthalene	Fluorene
2-Methylphenol	Naphthalene	2-Fluorobiphenyl (surr.)
4-Methylphenol	Nitrobenzene	Hexachlorocyclo-pentadiene
N-Nitrosodimethylamine	Nitrobenzene-d_8 (surr.)	1-Naphthylamine
N-Nitroso-di-n-propylamine	2-Nitrophenol	2-Naphthylamine
Phenol	N-Nitroso-di-n-butylamine	2-Nitroaniline
Phenol-d_6 (surr.)	N-Nitrosopiperidine	3-Nitroaniline
2-Picoline	1,2,4-Trichlorobenzene	4-Nitroaniline
		4-Nitrophenol
		Pentachlorobenzene
		1,2,4,5-Tetra-chlorobenzene
		2,3,4,6-Tetra-chlorophenol
		2,4,6-Tribromo-phenol (surr.)
		2,4,6-Trichloro-phenol
		2,4,5-Trichloro-phenol

(surr.) = surrogate

TABLE 5. SEMIVOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (Continued)

Phenanthrene-d_{10}	Chrysene-d_{12}	Perylene-d_{12}
4-Aminobiphenyl	Benzidine	Benzo(b)fluoranthene
Anthracene	Benzo(a)anthracene	Benzo(k)fluoranthene
4-Bromophenyl phenyl ether	Bis(2-ethylhexyl)phthalate	Benzo(g,h,i)perylene
Di-n-butyl phthalate	Butylbenzylphthalate	Benzo(a)pyrene
4,6-Dinitro-2-methylphenol	Chrysene	Dibenz(a,j)acridine
Diphenylamine	3,3'-Dichlorobenzidine	Dibenz(a,h)anthracene
1,2-Diphenylhydrazine	p-Dimethylaminoazobenzene	7,12-Dimethylbenz(a)anthracene
Fluoranthene	Pyrene	Di-n-octylphthalate
Hexachlorobenzene	Terphenyl-d_{14} (surr.)	Indeno(1,2,3-cd)pyrene
N-Nitrosodiphenylamine		3-Methylcholanthrene
Pentachlorophenol		
Pentachloronitrobenzene		
Phenacetin		
Phenanthrene		
Pronamide		

(surr.) = surrogate

7.6.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulas given above should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms and the RF for the compound should be assumed to be 1. The concentration obtained should be reported indicating (1) that the value is an estimate and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

7.6.2.4 Report results without correction for recovery data. When duplicates and spiked samples are analyzed, report all data obtained with the sample results.

7.6.2.5 Quantitation of multicomponent compounds (e.g., Aroclors) is beyond the scope of Method 8270. Normally, quantitation is performed using a GC/ECD by Method 8080.

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 water 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 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration standard 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.

8.4 Required instrument QC is found in the following sections:

8.4.1 The GC/MS system must be tuned to meet the DFTPP specifications in Section 7.3.1 and 7.4.1.

8.4.2 There must be an initial calibration of the GC/MS system as specified in 7.3.

8.4.3 The GC/MS system must meet the SPCC criteria specified in 7.4.3 and the CCC criteria in 7.4.4, each 12 hr.

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

8.5.1 A quality (QC) check sample concentrate is required containing each analyte at a concentration of 100 ug/mL in acetone. 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.

8.5.2 Using a pipet, prepare QC check samples at a concentration of 100 ug/L by adding 1.00 mL of QC check sample concentrate to each of four 1-L aliquots of reagent water.

8.5.3 Analyze the well-mixed QC check samples according to the method beginning in Section 7.1 with extraction of the samples.

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

8.5.5 For each analyte compare s and $\bar{X}$ with the corresponding acceptance criteria for precision and accuracy, respectively, found in Table 6. If s and $\bar{X}$ for all analytes 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 Table 6 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 analyzed.

8.5.6 When one or more of the analytes tested fail at least one of the acceptance criteria, the analyst must proceed according to Section 8.5.6.1 or 8.5.6.2.

8.5.6.1 Locate and correct the source of the problem and repeat the test for all analytes of interest beginning with Section 8.5.2.

TABLE 6. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	27.6	60.1-132.3	47-145
Acenaphthylene	100	40.2	53.5-126.0	33-145
Aldrin	100	39.0	7.2-152.2	D-166
Anthracene	100	32.0	43.4-118.0	27.133
Benzo(a)anthracene	100	27.6	41.8-133.0	33-143
Benzo(b)fluoranthene	100	38.8	42.0-140.4	24-159
Benzo(k)fluoranthene	100	32.3	25.2-145.7	11-162
Benzo(a)pyrene	100	39.0	31.7-148.0	17-163
Benzo(ghi)perylene	100	58.9	D-195.0	D-219
Benzyl butyl phthalate	100	23.4	D-139.9	D-152
β-BHC	100	31.5	41.5-130.6	24-149
δ-BHC	100	21.6	D-100.0	D-110
Bis(2-chloroethyl)ether	100	55.0	42.9-126.0	12-158
Bis(2-chloroethoxy)methane	100	34.5	49.2-164.7	33-184
Bis(2-chloroisopropyl)ether	100	46.3	62.8-138.6	36-166
Bis(2-ethylhexyl)phthalate	100	41.1	28.9-136.8	8-158
4-Bromophenyl phenyl ether	100	23.0	64.9-114.4	53-127
2-Chloronaphthalene	100	13.0	64.5-113.5	60-118
4-Chlorophenyl phenyl ether	100	33.4	38.4-144.7	25-158
Chrysene	100	48.3	44.1-139.9	17-168
4,4'-DDD	100	31.0	D-134.5	D-145
4,4'-DDE	100	32.0	19.2-119.7	4-136
4,4'-DDT	100	61.6	D-170.6	D-203
Dibenzo(a,h)anthracene	100	70.0	D-199.7	D-227
Di-n-butyl phthalate	100	16.7	8.4-111.0	1-118
1,2-Dichlorobenzene	100	30.9	48.6-112.0	32-129
1,3-Dichlorobenzene	100	41.7	16.7-153.9	D-172
1,4-Dichlorobenzene	100	32.1	37.3-105.7	20-124
3,3'-Dichlorobenzidine	100	71.4	8.2-212.5	D-262
Dieldrin	100	30.7	44.3-119.3	29-136
Diethyl phthalate	100	26.5	D-100.0	D-114
Dimethyl phthalate	100	23.2	D-100.0	D-112
2,4-Dinitrotoluene	100	21.8	47.5-126.9	39-139
2,6-Dinitrotoluene	100	29.6	68.1-136.7	50-158
Di-n-octylphthalate	100	31.4	18.6-131.8	4-146
Endosulfan sulfate	100	16.7	D-103.5	D-107
Endrin aldehyde	100	32.5	D-188.8	D-209
Fluoranthene	100	32.8	42.9-121.3	26-137
Fluorene	100	20.7	71.6-108.4	59-121
Heptachlor	100	37.2	D-172.2	D-192
Heptachlor epoxide	100	54.7	70.9-109.4	26.155
Hexachlorobenzene	100	24.9	7.8-141.5	D-152
Hexachlorobutadiene	100	26.3	37.8-102.2	24-116
Hexachloroethane	100	24.5	55.2-100.0	40-113

TABLE 6. QC ACCEPTANCE CRITERIA[a] - Continued

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Indeno(1,2,3-cd)pyrene	100	44.6	D-150.9	D-171
Isophorone	100	63.3	46.6-180.2	21-196
Naphthalene	100	30.1	35.6-119.6	21-133
Nitrobenzene	100	39.3	54.3-157.6	35-180
N-Nitrosodi-n-propylamine	100	55.4	13.6-197.9	D-230
PCB-1260	100	54.2	19.3-121.0	D-164
Phenanthrene	100	20.6	65.2-108.7	54-120
Pyrene	100	25.2	69.6-100.0	52-115
1,2,4-Trichlorobenzene	100	28.1	57.3-129.2	44-142
4-Chloro-3-methylphenol	100	37.2	40.8-127.9	22-147
2-Chlorophenol	100	28.7	36.2-120.4	23-134
2,4-Chlorophenol	100	26.4	52.5-121.7	39-135
2,4-Dimethylphenol	100	26.1	41.8-109.0	32-119
2,4-Dinitrophenol	100	49.8	D-172.9	D-191
2-Methyl-4,6-dinitrophenol	100	93.2	53.0-100.0	D-181
2-Nitrophenol	100	35.2	45.0-166.7	29-182
4-Nitrophenol	100	47.2	13.0-106.5	D-132
Pentachlorophenol	100	48.9	38.1-151.8	14-176
Phenol	100	22.6	16.6-100.0	5-112
2,4,6-Trichlorophenol	100	31.7	52.4-129.2	37-144

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 625. These criteria are based directly on the method performance data in Table 7. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 7.

8.5.6.2 Beginning with Section 8.5.2, 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 Section 8.5.2.

8.6 The laboratory must, on an ongoing basis, analyze a reagent blank, a matrix spike, and a matrix spike duplicate/duplicate for each analytical batch (up to a maximum of 20 samples/batch) to assess accuracy. For laboratories analyzing one to ten samples per month, at least one spiked sample per month is required.

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

8.6.1.1 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 Section 8.6.2, whichever concentration would be larger.

8.6.1.2 If the concentration of a specific analyte in the sample is not being checked against a limit specific to that analyte, the spike should be at 100 ug/L or 1 to 5 times higher than the background concentration determined in Section 8.6.2, whichever concentration would be larger.

8.6.1.3 If it is impractical to determine background levels before spiking (e.g., maximum holding times will be exceeded), the spike concentration should be at (1) the regulatory concentration limit, if any; or, if none (2) the larger of either 5 times higher than the expected background concentration or 100 ug/L.

8.6.2 Analyze one sample aliquot to determine the background concentration (B) of each analyte. If necessary, prepare a new QC check sample concentrate (Section 8.5.1) appropriate for the background concentration in the sample. Spike a second sample aliquot with 1.00 mL of the QC check 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.

8.6.3 Compare the percent recovery (p) for each analyte with the corresponding QC acceptance criteria found in Table 6. These acceptance criteria were calculated to include an allowance for error in measurement of both the background and spike concentrations, assuming a spike to background ratio of 5:1. This error will be accounted for to the extent that the analyst's spike to background ratio approaches 5:1. If spiking was performed at a concentration lower than 100 ug/L, the analyst must use either the QC acceptance criteria presented in Table 6, 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 Table 7, substituting the spike concentration (T) for C; (2) calculate overall precision (S') using the equation in Table 7, substituting x' for $\bar{x}$; (3) calculate the range for recovery at the spike concentration as $(100x'/T) \pm 2.44(100S'/T)\%$.

8.6.4 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 Section 8.7.

8.7 If any analyte fails the acceptance criteria for recovery in Section 8.6, a QC check standard containing each analyte that failed must be prepared and analyzed.

NOTE: The frequency for the required analysis of a QC check standard will depend upon the number of analytes being simultaneously tested, the complexity of the sample matrix, and the performance of the laboratory. If the entire list of analytes in Table 6 must be measured in the sample in Section 8.6, 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.

8.7.1 Prepare the QC check standard by adding 1.0 mL of the QC check sample concentrate (Section 8.5.1 or 8.6.2) to 1 L of reagent water. The QC check standard needs only to contain the analytes that failed criteria in the test in Section 8.6.

8.7.2 Analyzed the QC check standard 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.

8.7.3 Compare the percent recovery (p_s) for each analyte with the corresponding QC acceptance criteria found in Table 6. Only analytes that failed the test in Section 8.6 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 analytical result for that analyte in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

8.8 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) as in Section 8.6, 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).

8.9 To determine acceptable accuracy and precision limits for surrogate standards the following procedure should be performed.

TABLE 7. 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)
Acenaphthene	0.96C+0.19	0.15X-0.12	0.21X-0.67
Acenaphthylene	0.89C+0.74	0.24X-1.06	0.26X-0.54
Aldrin	0.78C+1.66	0.27X-1.28	0.43X+1.13
Anthracene	0.80C+0.68	0.21X-0.32	0.27X-0.64
Benzo(a)anthracene	0.88C-0.60	0.15X+0.93	0.26X-0.21
Chloroethane	0.99C-1.53	0.14X-0.13	0.17X-0.28
Benzo(b)fluoranthene	0.93C-1.80	0.22X+0.43	0.29X+0.96
Benzo(k)fluoranthene	0.87C-1.56	0.19X+1.03	0.35X+0.40
Benzo(a)pyrene	0.90C-0.13	0.22X+0.48	0.32X+1.35
Benzo(ghi)perylene	0.98C-0.86	0.29X+2.40	0.51X-0.44
Benzyl butyl phthalate	0.66C-1.68	0.18X+0.94	0.53X+0.92
β-BHC	0.87C-0.94	0.20X-0.58	0.30X+1.94
δ-BHC	0.29C-1.09	0.34X+0.86	0.93X-0.17
Bis(2-chloroethyl)ether	0.86C-1.54	0.35X-0.99	0.35X+0.10
Bis(2-chloroethoxy)methane	1.12C-5.04	0.16X+1.34	0.26X+2.01
Bis(2-chloroisopropyl)ether	1.03C-2.31	0.24X+0.28	0.25X+1.04
Bis(2-ethylhexyl)phthalate	0.84C-1.18	0.26X+0.73	0.36X+0.67
4-Bromophenyl phenyl ether	0.91C-1.34	0.13X+0.66	0.16X+0.66
2-Chloronaphthalene	0.89C+0.01	0.07X+0.52	0.13X+0.34
4-Chlorophenyl phenyl ether	0.91C+0.53	0.20X-0.94	0.30X-0.46
Chrysene	0.93C-1.00	0.28X+0.13	0.33X-0.09
4,4'-DDD	0.56C-0.40	0.29X-0.32	0.66X-0.96
4,4'-DDE	0.70C-0.54	0.26X-1.17	0.39X-1.04
4,4'-DDT	0.79C-3.28	0.42X+0.19	0.65X-0.58
Dibenzo(a,h)anthracene	0.88C+4.72	0.30X+8.51	0.59X+0.25
Di-n-butyl phthalate	0.59C+0.71	0.13X+1.16	0.39X+0.60
1,2-Dichlorobenzene	0.80C+0.28	0.20X+0.47	0.24X+0.39
1,3-Dichlorobenzene	0.86C-0.70	0.25X+0.68	0.41X+0.11
1,4-Dichlorobenzene	0.73C-1.47	0.24X+0.23	0.29X+0.36
3,3'-Dichlorobenzidine	1.23C-12.65	0.28X+7.33	0.47X+3.45
Dieldrin	0.82C-0.16	0.20X-0.16	0.26X-0.07
Diethyl phthalate	0.43C+1.00	0.28X+1.44	0.52X+0.22
Dimethyl phthalate	0.20C+1.03	0.54X+0.19	1.05X-0.92
2,4-Dinitrotoluene	0.92C-4.81	0.12X+1.06	0.21X+1.50
2,6-Dinitrotoluene	1.06C-3.60	0.14X+1.26	0.19X+0.35
Di-n-octylphthalate	0.76C-0.79	0.21X+1.19	0.37X+1.19
Endosulfan sulfate	0.39C+0.41	0.12X+2.47	0.63X-1.03
Endrin aldehyde	0.76C-3.86	0.18X+3.91	0.73X-0.62
Fluoranthene	0.81C+1.10	0.22X-0.73	0.28X-0.60
Fluorene	0.90C-0.00	0.12X+0.26	0.13X+0.61
Heptachlor	0.87C-2.97	0.24X-0.56	0.50X-0.23
Heptachlor epoxide	0.92C-1.87	0.33X-0.46	0.28X+0.64
Hexachlorobenzene	0.74C+0.66	0.18X-0.10	0.43X-0.52
Hexachlorobutadiene	0.71C-1.01	0.19X+0.92	0.26X+0.49
Hexachloroethane	0.73C-0.83	0.17X+0.67	0.17X+0.80

TABLE 7. METHOD ACCURACY AND PRECISION AS FUNCTIONS OF CONCENTRATION[a] - Continued

Parameter	Accuracy, as recovery, x' (ug/L)	Single analyst precision, s_r' (ug/L)	Overall precision, S' (ug/L)
Indeno(1,2,3-cd)pyrene	0.78C-3.10	0.29$\bar{X}$+1.46	0.50$\bar{X}$-0.44
Isophorone	1.12C+1.41	0.27$\bar{X}$+0.77	0.33$\bar{X}$+0.26
Naphthalene	0.76C+1.58	0.21$\bar{X}$-0.41	0.30$\bar{X}$-0.68
Nitrobenzene	1.09C-3.05	0.19$\bar{X}$+0.92	0.27$\bar{X}$+0.21
N-Nitrosodi-n-propylamine	1.12C-6.22	0.27$\bar{X}$+0.68	0.44$\bar{X}$+0.47
PCB-1260	0.81C-10.86	0.35$\bar{X}$+3.61	0.43$\bar{X}$+1.82
Phenanthrene	0.87C+0.06	0.12$\bar{X}$+0.57	0.15$\bar{X}$+0.25
Pyrene	0.84C-0.16	0.16$\bar{X}$+0.06	0.15$\bar{X}$+0.31
1,2,4-Trichlorobenzene	0.94C-0.79	0.15$\bar{X}$+0.85	0.21$\bar{X}$+0.39
4-Chloro-3-methylphenol	0.84C+0.35	0.23$\bar{X}$+0.75	0.29$\bar{X}$+1.31
2-Chlorophenol	0.78C+0.29	0.18$\bar{X}$+1.46	0.28$\bar{X}$+0.97
2,4-Dichlorophenol	0.87C-0.13	0.15$\bar{X}$+1.25	0.21$\bar{X}$+1.28
2,4-Dimethylphenol	0.71C+4.41	0.16$\bar{X}$+1.21	0.22$\bar{X}$+1.31
2,4-Dinitrophenol	0.81C-18.04	0.38$\bar{X}$+2.36	0.42$\bar{X}$+26.29
2-Methyl-4,6-dinitrophenol	1.04C-28.04	0.10$\bar{X}$+42.29	0.26$\bar{X}$+23.10
2-Nitrophenol	0.07C-1.15	0.16$\bar{X}$+1.94	0.27$\bar{X}$+2.60
4-Nitrophenol	0.61C-1.22	0.38$\bar{X}$+2.57	0.44$\bar{X}$+3.24
Pentachlorophenol	0.93C+1.99	0.24$\bar{X}$+3.03	0.30$\bar{X}$+4.33
Phenol	0.43C+1.26	0.26$\bar{X}$+0.73	0.35$\bar{X}$+0.58
2,4,6-Trichlorophenol	0.91C-0.18	0.16$\bar{X}$+2.22	0.22$\bar{X}$+1.81

x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in 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.

8.9.1 For each sample analyzed, calculate the percent recovery of each surrogate in the sample.

8.9.2 Once a minimum of thirty samples of the same matrix have been analyzed, calculate the average percent recovery (P) and standard deviation of the percent recovery (s) for each of the surrogates.

8.9.3 For a given matrix, calculate the upper and lower control limit for method performance for each surrogate standard. This should be done as follows:

$$\text{Upper Control Limit (UCL)} = p + 3s$$
$$\text{Lower Control Limit (LCL)} = p - 3s$$

8.9.4 For aqueous and soil matrices, these laboratory established surrogate control limits should, if applicable, be compared with the control limits listed in Table 8. The limits given in Table 8 are multi-laboratory performance based limits for soil and aqueous samples, and therefore, the single-laboratory limits established in Paragraph 8.9.3 must fall within those given in Table 8 for these matrices.

8.9.5 If recovery is not within limits, the following procedures are 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."

8.9.6 At a minimum, each laboratory should update surrogate recovery limits on a matrix-by-matrix basis, annually.

8.10 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.

TABLE 8. SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Low/Medium Water	Low/Medium Soil/Sediment
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

9.0 METHOD PERFORMANCE

9.1 Method 8250 was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-1,300 ug/L. Single operator accuracy and 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 7.

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, Method 625," October 26, 1984.

2. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

3. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, 58-63, 1983.

4. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry Systems," Analytical Chemistry, 47, 995-1000, 1975.

5. "Method Detection Limit for Methods 624 and 625," Olynyk, P., W.L. Budde, and J.W. Eichelberger, Unpublished report, October 1980.

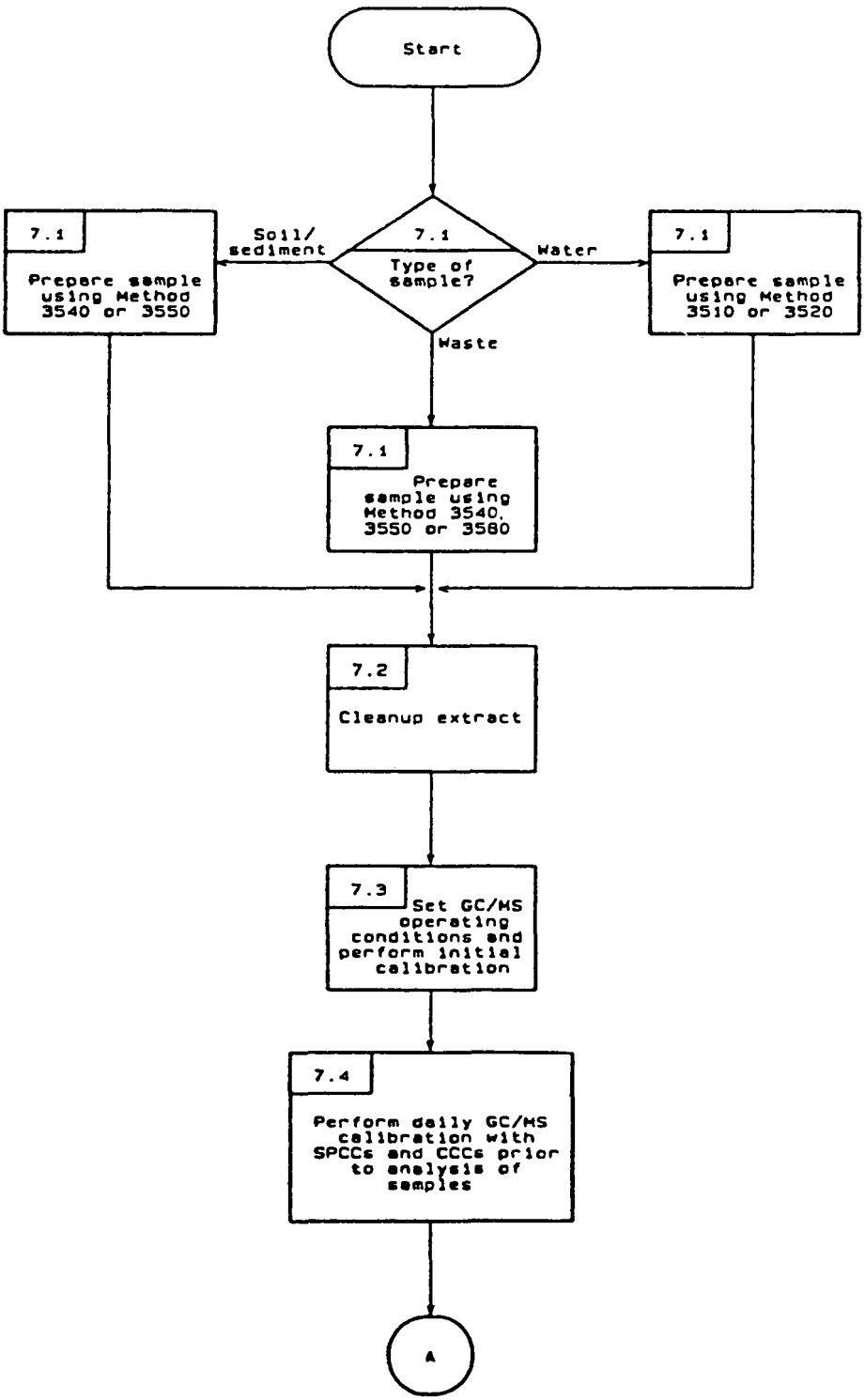
6. "Interlaboratory Method Study for EPA Method 625-Base/Neutrals, Acids, and Pesticides," Final Report for EPA Contract 68-03-3102 (in preparation).

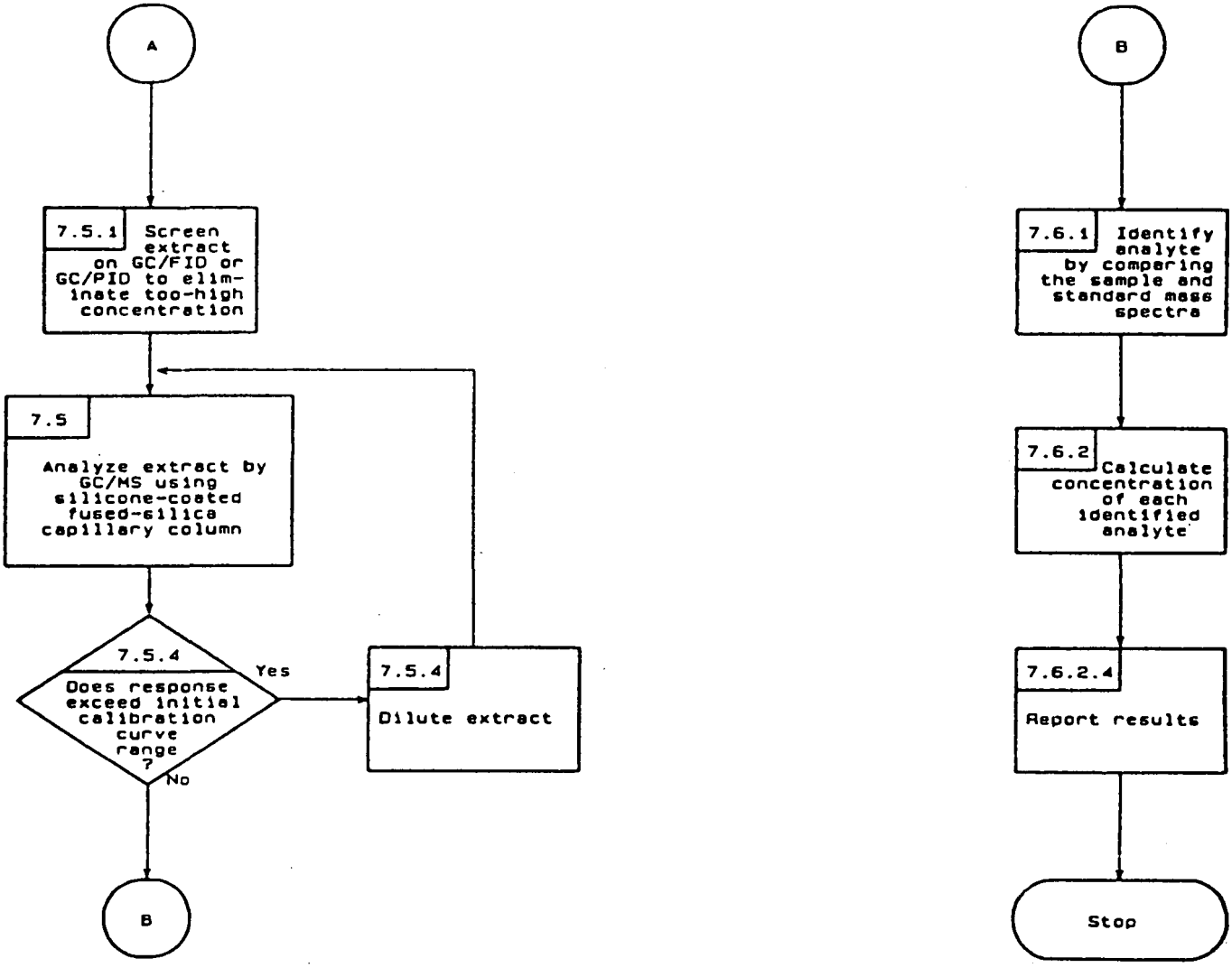
7. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

METHOD 8270

GAS CHROMATOGRAPHY/MASS SPECTROMETRY FOR SEMIVOLATILE ORGANICS:

CAPILLARY COLUMN TECHNIQUE




A
7.5.1 Screen extract on GC/FID or GC/PID to eliminate too-high concentration
7.5 Analyze extract by GC/MS using silicone-coated fused-silica capillary column
7.5.4 Does response exceed initial calibration curve range ?
Yes
No
7.5.4 Dilute extract
B
B
7.6.1 Identify analyte by comparing the sample and standard mass spectra
7.6.2 Calculate concentration of each identified analyte
7.6.2.4 Report results
Stop

METHOD 8280

THE ANALYSIS OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS

1.0 SCOPE AND APPLICATION

1.1 This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

1.2 The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposed quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

1.3 Certain 2,3,7,8-substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Special instructions are included which measure 2,3,7,8-substituted congeners.

1.4 This method is recommended for use only by analysts experienced with residue analysis and skilled in mass spectral analytical techniques.

1.5 Because of the extreme toxicity of these compounds, the analyst must take necessary precautions to prevent exposure to himself, or to others, of materials known or believed to contain PCDD's or PCDF's. Typical infectious waste incinerators are probably not satisfactory devices for disposal of materials highly contaminated with PCDD's or PCDF's. A laboratory planning to use these compounds should prepare a disposal plan to be reviewed and approved by EPA's Dioxin Task Force (Contact Conrad Kleveno, WH-548A, U.S. EPA, 401 M Street S.W., Washington, D.C. 20450). Additional safety instructions are outlined in Appendix B.

2.0 SUMMARY OF THE METHOD

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/low resolution mass spectrometry (HRGC/LRMS) techniques.

2.2 If interferents are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

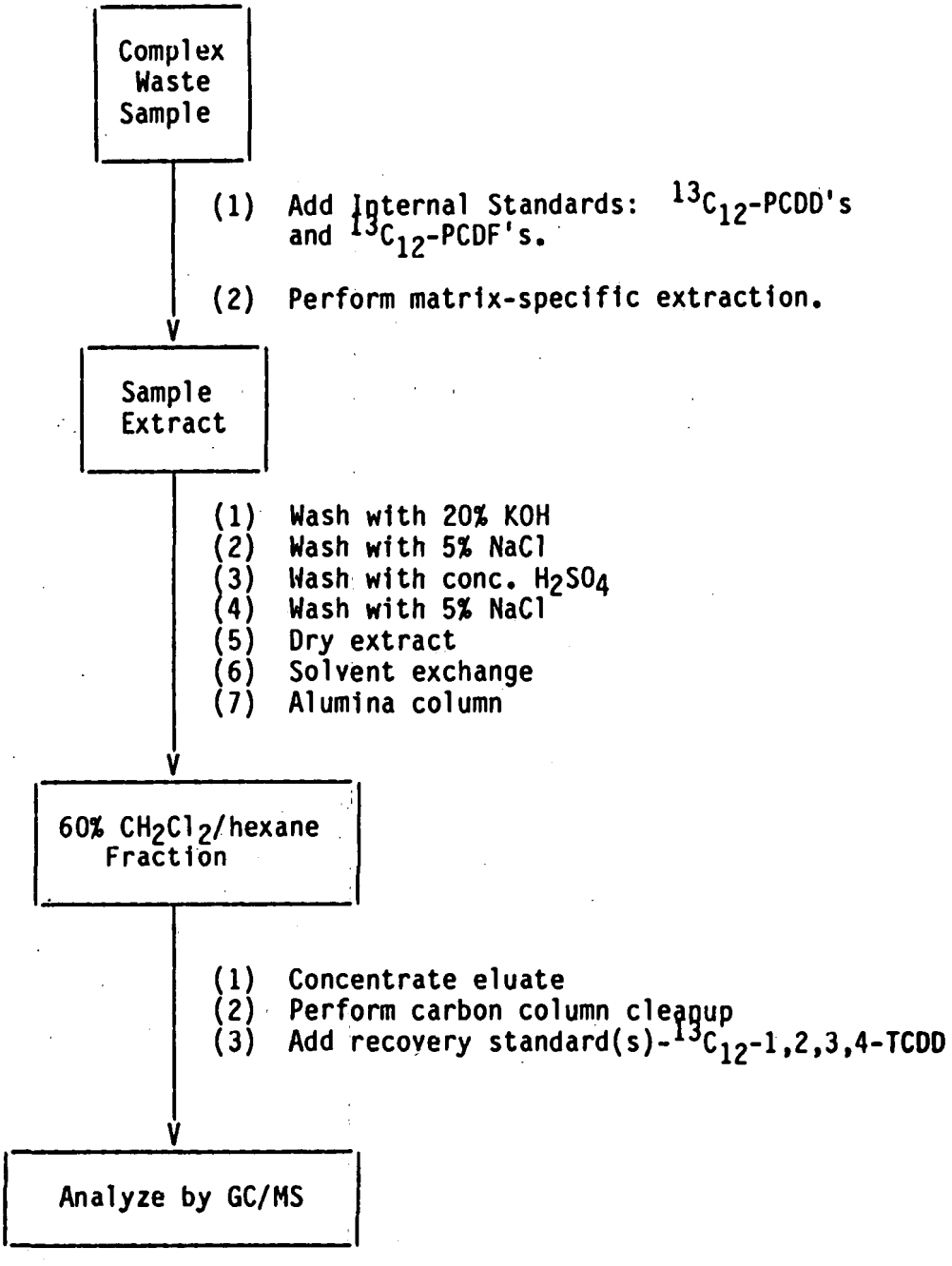


Figure 1. Method 8280 flow chart for sample extraction and cleanup as used for the analysis of PCDD's and PCDF's in complex waste samples.

3.0 INTERFERENCES

3.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

3.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all glass systems may be required.

3.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDD's and PCDF's are often associated with other interfering chlorinated compounds such as PCB's and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 6-3. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit (Section 11.6) stated in Table 8.

3.4 High resolution capillary columns are used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all of the isomers.

3.5 Aqueous samples cannot be aliquoted from sample containers. The entire sample must be used and the sample container washed/rinsed out with the extracting solvent.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment for discrete or composite sampling:

4.1.1 Grab sample bottle--amber glass, 1-liter or 1-quart volume. French or Boston Round design is recommended. The container must be acid washed and solvent rinsed before use to minimize interferences.

4.1.2 Bottle caps--threaded to screw onto the sample bottles. Caps must be lined with Teflon. Solvent washed foil, used with the shiny side toward the sample, may be substituted for Teflon if the sample is not corrosive. Apply tape around cap to completely seal cap to bottom.

4.1.3 Compositing equipment--automatic or manual compositing system. No tygon or rubber tubing may be used, and the system must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated after sampling.

4.2 Water bath--heated, with concentric ring cover, capable of temperature control (±2°C). The bath should be used in a hood.

4.3 Gas chromatograph/mass spectrometer data system:

4.3.1 **Gas chromatograph:** An analytical system with a temperature-programmable gas chromatograph and all required accessories including syringes, analytical columns, and gases.

4.3.2 Fused silica capillary columns are required. As shown in Table 1, three columns were evaluated using a column performance check mixture containing 1,2,3,4-TCDD, 2,3,7,8-TCDD, 1,2,3,4,7 PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, and 2,3,7,8-TCDF.

The columns include the following: (a) 50-m CP-Sil-88 programmed 60°-190° at 20°/minute, then 190°-240° at 5°/minute; (b) DB-5 (30-m x 0.25-mm I.D.; 0.25-um film thickness) programmed 170° for 10 minutes, then 170°-320° at 8°/minute, hold at 320°C for 20 minutes; (c) 30-m SP-2250 programmed 70°-320° at 10°/minute. Column/conditions (a) provide good separation of 2,3,7,8-TCDD from the other TCDD's at the expense of longer retention times for higher homologs. Column/conditions (b) and (c) can also provide acceptable separation of 2,3,7,8-TCDD. Resolution of 2,3,7,8-TCDD from the other TCDD's is better on column (c), but column (b) is more rugged, and may provide better separation from certain classes of interferents. Data presented in Figure 2 and Tables 1 to 8 of this Method were obtained using a DB-5 column with temperature programming described in (b) above. However, any capillary column which provides separation of 2,3,7,8-TCDD from all other TCDD isomers equivalent to that specified in Section 6.3 may be used; this separation must be demonstrated and documented using the performance test mixture described in Paragraph 6.3.

4.3.3 **Mass spectrometer:** A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 sec or less. Minimum integration time for SIM is 50 ms per m/z. The use of systems not capable of monitoring 11 ions simultaneously will require the analyst to make multiple injections.

4.3.4 **GC/MS interface:** Any GC-to-MS interface that gives an acceptable calibration response for each analyte of interest at the concentration required and achieves the required tuning performance criteria (see Paragraphs 6.1.-6.3) may be used. GC-to-MS interfaces constructed of all glass or glass-lined materials are required. Glass can be deactivated by silanizing with dichlorodimethylsilane. Inserting a fused silica column directly into the MS source is recommended; care must be taken not to expose the end of the column to the electron beam.

4.3.5 **Data system:** A computer system must be interfaced to the mass spectrometer. The system must allow for the continuous acquisition and storage on machine-readable media of all data obtained throughout the duration of the chromatographic program. The computer must have software that can search any GC/MS data file for ions of a specific mass and can plot such ion abundances versus time or scan number. This type of plot

is defined as an Selected Ion Current Profile (SICP). Software must also be able to integrate the abundance, in any SICP, between specified time or scan number limits.

4.4 Pipets-Disposable, Pasteur, 150-mm long x 5-mm I.D. (Fisher Scientific Company, No. 13-678-6A, or equivalent).

4.4.1 Pipet, disposable, serological 10-mL (American Scientific Products No. P4644-10, or equivalent) for preparation of the carbon column specified in Paragraph 4.19.

4.5 Amber glass bottle (500-mL, Teflon-lined screw-cap).

4.6 Reacti-vial 2-mL, amber glass (Pierce Chemical Company). These should be silanized prior to use.

4.7 500-mL Erlenmeyer flask (American Scientific Products Cat. No. f4295 500f0) fitted with Teflon stoppers (ASP No. s9058-8, or equivalent).

4.8 Wrist Action Shaker (VWR No. 57040-049, or equivalent).

4.9 125-mL and 2-L Separatory Funnels (Fisher Scientific Company, No. 10-437-5b, or equivalent).

4.10 500-mL Kuderna-Danish fitted with a 10-mL concentrator tube and 3-ball Snyder column (Ace Glass No. 6707-02, 6707-12, 6575-02, or equivalent).

4.11 Teflon boiling chips (Berghof/American Inc., Main St., Raymond, New Hampshire 03077, No. 15021-450, or equivalent). Wash with hexane prior to use.

4.12 300-mm x 10.5-mm glass chromatographic column fitted with Teflon stopcock.

4.13 15-mL conical concentrator tubes (Kontes No. K-288250, or equivalent).

4.14 Adaptors for concentrator tubes (14/20 to 19/22) (Ace Glass No. 9092-20, or equivalent).

4.15 Nitrogen blowdown apparatus (N-Evap (reg. trademark) Analytical Evaporator Model 111, Organomation Associates Inc., Northborough, Massachusetts or equivalent). Teflon tubing connection to trap and gas regulator is required.

4.16 Microflex conical vials 2.0-mL (Kontes K-749000, or equivalent).

4.17 Filter paper (Whatman No. 54, or equivalent). Glass fiber filters or glass wool plugs are also recommended.

4.18 Solvent reservoir (125-mL) Kontes: (special order item) 12.5-cm diameter, compatible with gravity carbon column.

4.19 Carbon column (gravity flow): Prepare carbon/silica gel packing material by mixing 5 percent (by weight) active carbon AX-21 (Anderson Development Co., Adrain, Michigan), pre-washed with methanol and dried in vacuo at 110°C and 95 percent (by weight) Silica gel (Type 60, EM reagent 70 to 230 mesh, CMS No. 393-066) followed by activation of the mixture at 130° for 6 hr. Prepare a 10-mL disposable serological pipet by cutting off each end to achieve a 4-in. column. Fire polish both ends; flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon/silica gel mixture. Cap the packing with a glass-wool plug. (Attach reservoir to column for addition of solvents).

Option: Carbon column (HPLC): A silanized glass HPLC column (10 mm x 7 cm), or equivalent, which contains 1 g of a packing prepared by mixing 5 percent (by weight) active carbon AX-21, (Anderson Development Co., Adrian, Michigan), washed with methanol and dried in vacuo at 110°C, and 95 percent (by weight) 10 um silica (Spherisorb S10W from Phase Separations, Inc., Norwalk, Connecticut). The mixture must then be stirred and sieved through a 38-um screen (U.S. Sieve Designation 400-mesh, American Scientific Products, No. S1212-400, or equivalent) to remove any clumps.[1]

4.20 HPLC pump with loop valve (1.0 mL) injector to be used in the optional carbon column cleanup procedure.

4.21 Dean-Stark trap, 5- or 10-mL with T joints, (Fisher Scientific Company, No. 09-146-5, or equivalent) condenser and 125-mL flask.

4.22 Continuous liquid-liquid extractor (Hershberg-Wolfe type, Lab Glass No. LG-6915; or equivalent.).

4.23 Roto-evaporator, R-110. Buchi/Brinkman - American Scientific No. E5045-10; or equivalent.

5.0 REAGENTS

5.1 Potassium hydroxide (ASC): 20 percent (w/v) in distilled water.

5.2 Sulfuric acid (ACS), concentrated.

5.3 Methylene chloride, hexane, benzene, petroleum ether, methanol, tridecane, isooctane, toluene, cyclohexane. Distilled in glass or highest available purity.

5.4 Prepare stock standards in a glovebox from concentrates or neat materials. The stock solutions (50 ppm) are stored in the dark at 4°C, and checked frequently for signs of degradation or evaporation, especially just prior to the preparation of working standards.

---

1 The carbon column preparation and use is adapted from W. A. Korfmacher, L. G. Rushing, D. M. Nestorick, H. C. Thompson, Jr., R. K. Mitchum, and J. R. Kominsky, Journal of High Resolution Chromatography and Chromatography Communications, 8, 12-19 (1985).

5.5 Alumina, neutral, Super 1, Woelm, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.

5.6 Prepurified nitrogen gas.

5.7 Anhydrous sodium sulfate (reagent grade): Extracted by manual shaking with several portions of hexane and dried at 100°C.

5.8 Sodium chloride - (analytical reagent), 5 percent (w/v) in distilled water.

6.0 CALIBRATION

6.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by results of routine calibration procedures described below. The other type, routine calibration, consists of analyzing the column performance check solution and a concentration calibration solution of 500 ng/mL (Paragraph 6.2). No samples are to be analyzed until acceptable calibration as described in Paragraphs 6.3 and 6.6 is demonstrated and documented.

6.2 Initial calibration:

6.2.1 Prepare multi-level calibration standards[2] keeping one of the recovery standards and the internal standard at fixed concentrations (500 ng/mL). Additional internal standards ($^{13}C_{12}$-OCDD 1,000 ng/mL) are recommended when quantification of the hepta- and octa-isomers is required. The use of separate internal standards for the PCDF's is also recommended. Each calibration standard should contain the following compounds:

2,3,7,8-TCDD,		
1,2,3,7,8-PeCDD	or any available	2,3,7,8,X-PeCDD isomer,
1,2,3,4,7,8-HxCDD	or any available	2,3,7,8,X,Y-HxCDD isomer,
1,2,3,4,6,7,8-HpCDD	or any available	2,3,7,8,X,Y,Z-HpCDD isomer,
2,3,7,8-TCDF		
1,2,3,7,8,PeCDF	or any available	2,3,7,8,X-PeCDF isomer,
1,2,3,4,7,8-HxCDF	or any available	2,3,7,8,X,Y,HxCDF isomer,
1,2,3,4,6,7,8-HpCDF	or any available	2,3,7,8,X,Y,Z-HpCDF isomer,

OCDD, OCDF, $^{13}C_{12}$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-OCDD.

---

2 $^{13}C_{12}$-labeled analytes are available from Cambridge Isotope Laboratory, Woburn, Massachusetts. Proper quantification requires the use of a specific labeled isomer for each congener to be determined. When labeled PCDD's and PCDF's of each homolog are available, their use will be required consistent with the technique of isotopic dilution.

Recommended concentration levels for standard analytes are 200, 500, 1,000, 2,000, and 5,000 ng/mL. These values may be adjusted in order to insure that the analyte concentration falls within the calibration range. Two uL injections of calibration standards should be made. However, some GC/MS instruments may require the use of a 1-uL injection volume; if this injection volume is used then all injections of standards, sample extracts and blank extracts must also be made at this injection volume. Calculation of relative response factors is described in Paragraph 11.1.2. Standards must be analyzed using the same solvent as used in the final sample extract. A wider calibration range is useful for higher level samples provided it can be described within the linear range of the method, and the identification criteria defined in Paragraph 10.4 are met. All standards must be stored in an isolated refrigerator at 4°C and protected from light. Calibration standard solutions must be replaced routinely after six months.

6.3 Establish operating parameters for the GC/MS system; the instrument should be tuned to meet the isotopic ratio criteria listed in Table 3 for PCDD's and PCDF's. Once tuning and mass calibration procedures have been completed, a column performance check mixture[3] containing the isomers listed below should be injected into the GC/MS system:

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

Because of the known overlap between the late-eluting tetra-isomers and the early-eluting penta-isomers under certain column conditions, it may be necessary to perform two injections to define the TCDD/TCDF and PeCDD/PeCDF elution windows, respectively. Use of this performance check mixture will enable the following parameters to be checked: (a) the retention windows for each of the homologues, (b) the GC resolution of 2,3,7,8-TCDD and 1,2,3,4-TCDD, and (c) the relative ion abundance criteria listed for PCDD's and PCDF's in Table 3. GC column performance should be checked daily for resolution and peak shape using this check mixture.

The chromatographic peak separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD must be resolved with a valley of $\leq$25 percent, where

$$\text{Valley Percent} = (x/y)\ (100)$$

x = measured as in Figure 2
y = the peak height of 2,3,7,8-TCDD

---

3 Performance check mixtures are available from Brehm Laboratory, Wright State University, Dayton, Ohio.

It is the responsibility of the laboratory to verify the conditions suitable for maximum resolution of 2,3,7,8-TCDD from all other TCDD isomers. The peak representing 2,3,7,8-TCDD should be labeled and identified as such on all chromatograms.

6.4 Acceptable SIM sensitivity is verified by achieving a minimum signal-to-noise ratio of 50:1 for the m/z 320 ion of 2,3,7,8-TCDD obtained from injection of the 200 ng/mL calibration standard.

6.5 From injections of the 5 calibration standards, calculate the relative response factors (RRF's) of analytes vs. the appropriate internal standards, as described in Paragraph 11.1.2. Relative response factors for the hepta- and octa-chlorinated CDD's and CDF's are to be calculated using the corresponding $^{13}C_{12}$-octachlorinated standards.

6.6 For each analyte calculate the mean relative response factor (RRF), the standard deviation, and the percent relative standard deviation from triplicate determinations of relative response factors for each calibration standard solution.

6.7 The percent relative standard deviations (based on triplicate analysis) of the relative response factors for each calibration standard solution should not exceed 15 percent. If this condition is not satisfied, remedial action should be taken.

6.8 The Laboratory must not proceed with analysis of samples before determining and documenting acceptable calibration with the criteria specified in Paragraphs 6.3 and 6.7.

6.9 Routine calibration:

6.9.1 Inject a 2-uL aliquot of the column performance check mixture. Acquire at least five data points for each GC peak and use the same data acquisition time for each of the ions being monitored.

NOTE: The same data acquisition parameters previously used to analyze concentration calibration solutions during initial calibration must be used for the performance check solution. The column performance check solution must be run at the beginning and end of a 12 hr period. If the contractor laboratory operates during consecutive 12-hr periods (shifts), analysis of the performance check solution at the beginning of each 12-hr period and at the end of the final 12-hr period is sufficient.

Determine and document acceptable column performance as described in Paragraph 6.3.

6.9.2 Inject a 2-uL aliquot of the calibration standard solution at 500 ng/mL at the beginning of a 2-hr period. Determine and document acceptable calibration as specified in Paragraph 6.3, i.e., SIM sensitivity and relative ion abundance criteria. The measured RRF's of

all analytes must be within +30 percent of the mean values established by initial analyses of the calibration standard solutions.

7.0 QUALITY CONTROL

7.1 Before processing any samples, the analyst must demonstrate through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

7.2 A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

7.3 The laboratory will be expected to analyze performance evaluation samples as provided by the EPA on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

7.4 Samples may be split with other participating labs on a periodic basis to ensure interlaboratory consistency. At least one sample per set of 24 must be run in duplicate to determine intralaboratory precision.

7.5 Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab).

7.6 Where appropriate, "field blanks" will be provided to monitor for possible cross-contamination of samples in the field. The typical "field blank" will consist of uncontaminated soil (background soil taken off-site).

7.7 GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

7.8 Before using any cleanup procedure, the analyst must process a series of calibration standards (Paragraph 6.2) through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes.

NOTE: This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

8.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of tygon, rubber tubing, other potential sources of contamination which may absorb the target analytes.

8.2 All samples must be stored at 4°C, extracted within 30 days and completely analyzed within 45 days of collection.

9.0 EXTRACTION AND CLEANUP PROCEDURES

9.1 Internal standard addition. Use a sample aliquot of 1 g to 1,000 mL (typical sample size requirements for each type of matrix are provided in Paragraph 9.2) of the chemical waste or soil to be analyzed. Transfer the sample to a tared flask and determine the weight of the sample. Add an appropriate quantity of $^{13}C_{12}$-2,3,7,8-TCDD, and any other material which is to be used as an internal standard, (Paragraph 6.2). All samples should be spiked with at least one internal standard, for example, $^{13}C_{12}$-2,3,7,8-TCDD, to give a concentration of 500 ng/mL in the final concentrated extract. As an example, a 10 g sample concentrated to a final volume of 100 uL requires the addition of 50 ng of $^{13}C_{12}$-2,3,7,8-TCDD, assuming 100% recovery. Adoption of different calibration solution sets (as needed to achieve different quantification limits for different congeners) will require a change in the fortification level. Individual concentration levels for each homologous series must be specified.

9.2 Extraction

9.2.1 **Sludge/fuel oil.** Extract aqueous sludge samples by refluxing a sample (e.g. 2 g) with 50 mL of toluene (benzene) in a 125-mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water has been removed. Cool the sample, filter the toluene extract through a fiber filter, or equivalent, into a 100-mL round bottom flask. Rinse the filter with 10 mL of toluene, combine the extract and rinsate. Concentrate the combined solution to near dryness using a rotary evaporator at 50°C. Use of an inert gas to concentrate the extract is also permitted. Proceed with Step 9.2.4.

9.2.2 **Still bottom.** Extract still bottom samples by mixing a sample (e.g., 1.0 g) with 10 mL of toluene (benzene) in a small beaker and filtering the solution through a glass fiber filter (or equivalent) into a 50-mL round bottom flask. Rinse the beaker and filter with 10 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C while connected to a water aspirator. Proceed with Step 9.2.4.

9.2.3 **Fly ash.** Extract fly ash samples by placing a sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a Soxhlet extraction apparatus charged with 100 mL of toluene (benzene) and extract for 16 hr using a three cycle/hour schedule. Cool and filter the toluene extract through a glass fiber filter paper into a 500-mL round bottom flask. Rinse the filter with 5 mL of toluene. Concentrate the combined toluene solution to near dryness using a rotary evaporator at 50°C. Proceed with Step 9.2.4.

9.2.4 Transfer the residue to a 125-mL separatory funnel using 15 mL of hexane. Rinse the flask with two 5-mL aliquots of hexane and add the rinses to the funnel. Shake 2 min with 50 mL of 5% NaCl solution, discard the aqueous layer and proceed with Step 9.3.

9.2.5 **Soil.** Extract soil samples by placing the sample (e.g. 10 g) and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hr. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

9.2.5.1 Filter the extract from Paragraph 9.2.5 through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (KD) concentrator fitted with a 10-mL concentrator tube. Add 50 mL of petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional 50-mL aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional 5-mL portions of petroleum ether.

9.2.5.2 Add a Teflon or PFTE boiling chip and a three-ball Snyder column to the KD flask. Concentrate in a 70°C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 min.

9.2.5.3 Add 50 mL of hexane and a new boiling chip to the KD flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 min.

9.2.5.4 Remove and invert the Snyder column and rinse it down into the KD with two 1-mL portions of hexane. Decant the contents of the KD and concentrator tube into a 125-mL separatory funnel. Rinse the KD with two additional 5-mL portions of hexane, combine. Proceed with Step 9.3.

9.2.6 **Aqueous samples:** Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume.

Pour the entire sample (approximately 1-L) into a 2-L separatory funnel. Proceed with Step 9.2.6.1.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel when experience with a sample from a given source indicates that a serious emulsion problem will result or an emulsion is encountered using a separatory funnel. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 sec to rinse the inner surface. Transfer the solvent to the extractor. Repeat the sample bottle rinse with an additional 50- to 100-mL portion of methylene chloride and add the rinse to the extractor. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hr. Allow to cool, then detach the distilling flask. Dry and concentrate the extract as described in Paragraphs 9.2.6.1 and 9.2.6.2. Proceed with Paragraph 9.2.6.3.

9.2.6.1 Add 60 mL methylene chloride to the sample bottle, seal and shake 30 sec to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer.

9.2.6.2 Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint with 2 x 5 mL hexane and combine rinses with extract to give a final volume of about 15 mL.

9.2.6.3 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with Paragraph 9.3.

9.3 In a 250-mL Separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 min.

Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times). Strong base (KOH) is known to degrade certain PCDD/PCDF's, contact time must be minimized.

9.4 Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard aqueous layer (bottom).

NOTE: Care should be taken due to the heat of neutralization and hydration.

9.5 Partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 min. Remove and discard the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer. (Perform acid washings a maximum of four times.)

9.6 Partition the extract against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 min. Remove and discard the aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing anhydrous sodium sulfate into a 50-mL round bottom flask, wash the separatory funnel with two 15-mL portions of hexane, pour through the funnel, and combine the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (35°C water bath), making sure all traces of toluene are removed. (Use of blowdown with an inert gas to concentrate the extract is also permitted).

9.7 Pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon stopcock, in the following manner:

Insert a glass-wool plug into the bottom of the column. Add a 4-g layer of sodium sulfate. Add a 4-g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed desiccator. Add a 4-g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present discard the column. Do not tap a wetted column.

9.8 Dissolve the residue from Step 9.6 in 2 mL of hexane and apply the hexane solution to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluant.

9.8.1 Elute with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDD's or PCDF's are eluted in this fraction. See Paragraph 9.9.1.

9.8.2 Elute the PCDD's and PCDF's from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this fraction in a conical shaped (15-mL) concentrator tube.

9.9 Carbon column cleanup:

Prepare a carbon column as described in Paragraph 4.18.

9.9.1 Using a carefully regulated stream of nitrogen (Paragraph 4.15), concentrate the 8 percent fraction from the alumina column (Paragraph 9.8.1) to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDD's and PCDF's. Concentrate the 60 percent fraction (Paragraph 9.8.2) to about 2 to 3 mL. Rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of cyclohexane/methylene chloride (50:50 v/v) and 5 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine (this fraction may be used as a check on column efficiency). Now turn the column over and in the direction of forward flow elute the PCDD/PCDF fraction with 20 mL toluene.

NOTE: Be sure no carbon fines are present in the eluant.

9.9.2 Alternate carbon column cleanup. Proceed as in Section 9.9.1 to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to an HPLC injector loop (1 mL). The injector loop is connected to the optional column described in Paragraph 4.18. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column. Elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant. Backflush the column with 40 mL toluene to elute and collect PCDD's and PCDF's (entire fraction). The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

9.9.3 Evaporate the toluene fraction to about 1 mL on a rotary evaporator using a water bath at 50°C. Transfer to a 2.0-mL Reacti-vial using a toluene rinse and concentrate to the desired volume using a stream of N_2. The final volume should be 100 uL for soil samples and 500 uL for sludge, still bottom, and fly ash samples; this is provided for guidance, the correct volume will depend on the relative concentration of target analytes. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted. Gently swirl the solvent on the lower portion of the vessel to ensure complete dissolution of the PCDD's and PCDF's.

9.10 Approximately 1 hr before HRGC/LRMS analysis, transfer an aliquot of the extract to a micro-vial (Paragraph 4.16). Add to this sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to give a concentration of 500 ng/mL. (Example: 36 uL aliquot of extract and 4 uL of recovery standard solution. Remember to adjust the final result to correct for this dilution. Inject an appropriate aliquot (1 or 2 uL) of the sample into the GC/MS instrument.

10.0 GC/MS ANALYSIS

10.1 When toluene is employed as the final solvent use of a bonded phase column from Paragraph 4.3.2 is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns (CP-Sil-88).

NOTE: Chromatographic conditions must be adjusted to account for solvent boiling points.

10.2 Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD (see Section 11). Add the recovery standard ($^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

10.3 Analyze samples with selected ion monitoring, using all of the ions listed in Table 2. It is recommended that the GC/MS run be divided into five selected ion monitoring sections, namely: (1) 243, 257,, 304, 306, 320, 322, 332, 334, 340, 356, 376 (TCDD's, TCDF's, $^{13}C_{12}$-labeled internal and recovery standards, PeCDD's, PeCDF's, HxCDE); (2) 277, 293, 306, 332, 338, 340, 342, 354, 356, 358, 410 (peCDD's, PeCDF's, HpCDE); (3) 311, 327, 340, 356, 372, 374, 376, 388, 390, 392, 446, (HxCDD's, HxCDF's, OCDE); (4) 345, 361, 374, 390, 406, 408, 410, 422, 424, 426, 480 (HpCDD's, HpCDF's, NCDE) and (5) 379, 395, 408, 424, 442, 444, 458, 460, 470, 472, 514 (OCDD, OCDF, $^{13}C_{12}$-OCDD, DCDE). Cycle time not to exceed 1 sec/descriptor. It is recommended that selected ion monitoring section 1 should be applied during the GC run to encompass the retention window (determined in Paragraph 6.3) of the first- and last-eluting tetra-chlorinated isomers. If a response is observed at m/z 340 or 356, then the GC/MS analysis must be repeated; selected ion monitoring section 2 should then be applied to encompass the retention window of the first- and last-eluting penta-chlorinated isomers. HxCDE, HpCDE, OCDE, NCDE, DCDE, are abbreviations for hexa-, hepta-, octa-, nona-, and decachlorinated diphenyl ether, respectively.

10.4 Identification criteria for PCDD's and PCDF's:

10.4.1 All of the characteristic ions, i.e. quantitation ion, confirmation ions, listed in Table 2 for each class of PCDD and PCDF, must be present in the reconstructed ion chromatogram. It is desirable that the M - COCl ion be monitored as an additional requirement. Detection limits will be based on quantitation ions within the molecules in cluster.

10.4.2 The maximum intensity of each of the specified characteristic ions must coincide within 2 scans or 2 sec.

10.4.3 The relative intensity of the selected, isotopic ions within the molecular ion cluster of a homologous series of PCDD's of PCDF's must lie within the range specified in Table 3.

10.4.4 The GC peaks assigned to a given homologous series must have retention times within the window established for that series by the column performance solution.

10.5 Quantitate the PCDD and PCDF peaks from the response relative to the appropriate internal standard. Recovery of each internal standard) vs. the recovery standard must be greater than 40 percent. It is recommended that samples with recoveries of less than 40 percent or greater than 120 percent be re-extracted and re-analyzed.

NOTE: These criteria are used to assess method performance; when properly applied, isotope dilution techniques are independent of internal standard recovery.

In those circumstances where these procedures do not yield a definitive conclusion, the use of high resolution mass spectrometry or HRGC/MS/MS is suggested.

11.0 CALCULATIONS

NOTE: The relative response factors of a given congener within any homologous series are known to be different. However, for purposes of these calculations, it will be assumed that every congener within a given series has the same relative response factor. In order to minimize the effect of this assumption on risk assessment, a 2,3,7,8-substituted isomer that is commercially available was chosen as representative of each series. All relative response factor calculations for a given homologous series are based on that compound.

11.1 Determine the concentration of individual isomers of tetra-, penta, and hexa-CDD/CDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-2,3,7,8-TCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 334) of the internal standard, $^{13}C_{12}$-2,3,7,8-TCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 334 of $^{13}C_{12}$-2,3,7,8-TCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.1 Determine the concentration of individual isomers of hepta-CDD/CDF and the concentration of OCDD and OCDF according to the equation:

$$\text{Concentration, ng/g} = \frac{Q_{is} \times A_s}{G \times A_{is} \times RRF}$$

where:

Q_{is} = ng of internal standard $^{13}C_{12}$-OCDD, added to the sample before extraction.

G = g of sample extracted.

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion (m/z 472) of the internal standard, $^{13}C_{12}$-OCDD.

RRF = response factor of the quantitation ion of the compound of interest relative to m/z 472 of $^{13}C_{12}$-OCDD.

NOTE: Any dilution factor introduced by following the procedure in Paragraph 9.10 should be applied to this calculation.

11.1.2 Relative response factors are calculated using data obtained from the analysis of multi-level calibration standards according to the equation:

$$RRF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = area of quantitation ion of the compound of interest.

A_{is} = area of quantitation ion of the appropriate internal standard (m/z 334 for $^{13}C_{12}$-2,3,7,8-TCDD; m/z 472 for $^{13}C_{12}$-OCDD).

C_{is} = concentration of the appropriate internal standard, $^{13}C_{12}$-2,3,7,8-TCDD or $^{13}C_{12}$-OCDD)

C_s = concentration of the compound of interest.

11.1.3 The concentrations of unknown isomers of TCDD shall be calculated using the mean RRF determined for 2,3,7,8-TCDD.

The concentrations of unknown isomers of PeCDD shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDD or any available 2,3,7,8,X-PeCDD isomer.

The concentrations of unknown isomers of HxCDD shall be calculated using the mean RRF determined for 1,2,3,4,7,8-HxCDD or any available 2,3,7,8,-X,Y-HXCDD isomer.

The concentrations of unknown isomers of HpCDD shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDD or any available 2,3,7,8,X,Y,Z-HpCDD isomer.

The concentrations of unknown isomers of TCDF shall be calculated using the mean RRF determined for 2,3,7,8-TCDF.

The concentrations of unknown isomers of PeCDF shall be calculated using the mean RRF determined for 1,2,3,7,8-PeCDF or any available 2,3,7,8,X-PeCDF isomer.

The concentrations of unknown isomers of HxCDF shall be calculated using the mean RRF determined for 1,2,4,7,8-HxCDF or any available 2,3,7,8-X,Y-HxCDF isomer.

The concentrations of unknown isomers of HpCDF shall be calculated using the mean RRF determined for 1,2,3,4,6,7,8-HpCDF or any available 2,3,7,8,X,Y,Z-HpCDF isomer.

The concentration of the octa-CDD and octa-CDF shall be calculated using the mean RRF determined for each.

Mean relative response factors for selected PCDD's and PCDF's are given in Table 4.

11.1.4 Calculate the percent recovery, R_{is}, for each internal standard in the sample extract, using the equation:

$$R_{is} = \frac{A_{is} \times Q_{rs}}{A_{rs} \times RF_r \times Q_{is}} = 100\%$$

where:

A_{rs} = Area of quantitation ion (m/z 334) of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

Q_{rs} = ng of recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD, added to extract.

The response factor for determination of recovery is calculated using data obtained from the analysis of the multi-level calibration standards according to the equation:

$$RF_r = \frac{A_{is} \times C_{rs}}{A_{rs} \times C_{is}}$$

where:

C_{rs} = Concentration of the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD.

11.1.5 Calculation of total concentration of all isomers within each homologous series of PCDD's and PCDF's.

Total concentration of PCDD's or PCDF's = Sum of the concentrations of the individual PCDD or PCDF isomers

11.4 Report results in nanograms per gram; when duplicate and spiked samples are reanalyzed, all data obtained should be reported.

11.5 Accuracy and Precision. Table 5 gives the precision data for revised Method 8280 for selected analytes in the matrices shown. Table 6 lists recovery data for the same analyses. Table 2 shows the linear range and variation of response factors for selected analyte standards. Table 8 provides the method detection limits as measured in specific sample matrices.

11.6 Method Detection Limit. The Method Detection Limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The procedure used to determine the MDL values reported in Table 8 was obtained from Appendix A of EPA Test Methods manual, EPA-600/4-82-057 July 1982, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater."

11.7 Maximum Holding Time (MHT). Is that time at which a 10 percent change in the analyte concentration (C_{t10}) occurs and the precision of the method of measurement allows the 10 percent change to be statistically different from the 0 percent change (C_{t0}) at the 90 percent confidence level. When the precision of the method is not sufficient to statistically discriminate a 10 percent change in the concentration from 0 percent change, then the maximum holding time is that time where the percent change in the analyte concentration (C_{tn}) is statistically different than the concentration at 0 percent change (C_{t0}) and greater than 10 percent change at the 90 percent confidence level.

TABLE 1. REPRESENTATIVE GAS CHROMATOGRAPH RETENTION TIMES* OF ANALYTES

Analyte	50-m CP-Sil-88	30-m DB-5	3--m SP-2250
2,3,7,8-TCDF	25.2	17.8	26.7
2,3,7,8-TCDD	23.6	17.4	26.7
1,2,3,4-TCDD	24.1	17.3	26.5
1,2,3,4,7-PeCDD	30.0	20.1	28.1
1,2,3,4,7,8-HxCDD	39.5	22.1	30.6
1,2,3,4,6,7,8-HpCDD	57.0	24.1	33.7
OCDD	NM	25.6	NM

*Retention time in min, using temperature programs shown below.

NM = not measured.

Temperature Programs:

CP-Sil-88	60°C-190°C at 20°/min; 190°-240° at 5°/min.
DB-5 30 m x 0.25 mm Thin film (0.25 um)	170°, 10 min; then at 8°/min to 320°C, hold at 320°C 20 min (until OCDD elutes).
SP-2250	70°-320° at 10°/minute.

Column Manufacturers

CP-Sil-88	Chrompack, Incorporated, Bridgewater, New Jersey
DB-5,	J and W Scientific, Incorporated, Rancho Cordova, California
SP-2250	Supelco, Incorporated, Bellefonte, Pennsylvania

TABLE 2. IONS SPECIFIED[a] FOR SELECTED ION MONITORING FOR PCDD'S AND PCDF'S

	Quantitation ion	Confirmation ions	M-COCl
PCDD's			
$^{13}C_{12}$-Tetra	334	332	---
Tetra	322	320	257
Penta	356	354;358	293
Hexa	390	388;392	327
Hepta	424	422;426	361
Octa	460	458	395
$^{13}C_{12}$-Octa	472	470	
PCDF's			
Tetra	306	304	243
Penta	340	338;342	277
Hexa	374	372;376	311
Hepta	408	406;410	345
Octa	444	442	379

[a]Ions at m/z 376 (HxCDE), 410 (HpCDE), 446 (OCDE), 480 (NCDE) and 514 (DCDE) are also included in the scan monitoring sections (1) to (5), respectively. See Paragraph 10.3.

TABLE 3. CRITERIA FOR ISOTOPIC RATIO MEASUREMENTS FOR PCDD'S AND PCDF'S

	Selected ions (m/z)	Relative intensity
PCDD's		
Tetra	320/322	0.65-0.89
Penta	358/356	0.55-0.75
Hexa	392/390	0.69-0.93
Hepta	426/424	0.83-1.12
Octa	458/460	0.75-1.01
PCDF's		
Tetra	304/306	0.65-0.89
Penta	342/340	0.55-0.75
Hexa	376/374	0.69-0.93
Hepta	410/408	0.83-1.12
Octa	442/444	0.75-1.01

TABLE 4. MEAN RELATIVE RESPONSE FACTORS OF CALIBRATION STANDARDS

Analyte	RRF[a]	RSD% (n = 5)	Quantitation ion (m/z)
2,3,7,8-TCDD	1.13	3.9	322
1,2,3,7,8-PeCDD	0.70	10.1	356
1,2,3,4,7,8-HxCDD	0.51	6.6	390
1,2,3,4,6,7,8-HpCDD[b]	1.08	6.6	424
OCDD[b]	1.30	7.2	460
2,3,7,8-TCDF	1.70	8.0	306
1,2,3,7,8-PeCDF	1.25	8.7	340
1,2,3,4,7,8-HxCDF	0.84	9.4	374
1,2,3,4,6,7,8-HpCDF[b]	1.19	3.8	444
OCDF[b]	1.57	8.6	408
$^{13}C_{12}$-2,3,7,8-TCDD	1.00	-	334
$^{13}C_{12}$-1,2,3,4-TCDD	0.75	4.6	334
$^{13}C_{12}$-OCDD	1.00	-	472

[a]The RRF value is the mean of the five determinations made. Nominal weights injected were 0.2, 0.5, 1.0, 2.0 and 5.0 ng.

[b]RRF values for these analytes were determined relative to $^{13}C_{12}$-OCDD. All other RRF's were determined relative to $^{13}C_{12}$-2,3,7,8-TCDD.

Instrument Conditions/Tune - GC/MS system was tuned as specified in Paragraph 6.3. RRF data was acquired under SIM control, as specified in Paragraph 10.3.

GC Program - The GC column temperature was programmed as specified in Paragraph 4.3.2(b).

TABLE 5. PRECISION DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
2,3,7,8-TCDD	clay	ND[b]	5.0	4	4.4
	soil	378	378	4	2.8
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom	487	487	4	24
1,2,3,4-TCDD	clay	ND	5.0	3	1.7
	soil	ND	25.0	4	1.1
	sludge	ND	125	4	9.0
	fly ash	38.5	38.5	4	7.9
	still bottom	ND	2500	4	-
1,3,6,8-TCDD	clay	ND	2.5	4	7.0
	soil	ND	25.0	4	5.1
	sludge	ND	125	4	3.1
	fly ash	19.1	19.1	2	-
	still bottom	227	2727	2	-
1,3,7,9-TCDD	clay	ND	2.5	4	19
	soil	ND	25.0	4	2.3
	sludge	ND	125.0	4	6.5
	fly ash	58.4	58.4	2	-
	still bottom	ND	2500	2	-
1,3,7,8-TCDD	clay	ND	5.0	4	7.3
	soil	ND	25.0	4	1.3
	sludge	ND	125	4	5.8
	fly ash	16.0	16.0	4	3.5
	still bottom	422	2920	2	-
1,2,7,8-TCDD	clay	ND	5.0	4	7.7
	soil	ND	25.0	4	9.0
	sludge	ND	125	4	7.7
	fly ash	2.6	2.6	3	23
	still bottom	ND	2500	2	-
1,2,8,9-TCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	0.6
	sludge	ND	125	4	1.9
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-

TABLE 5 (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
1,2,3,4,7-PeCDD	clay	ND	5.0	4	10
	soil	ND	25.0	4	2.8
	sludge	ND	125	4	4.6
	fly ash	25.8	25.8	2	6.9
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDD	clay	ND	5.0	4	25
	soil	ND	25.0	4	20
	sludge	ND	125	4	4.7
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,7,8-HxCDD	clay	ND	5.0	4	38
	soil	ND	25.0	4	8.8
	sludge	ND	125	4	3.4
	fly ash	ND	46	2	-
	still bottom	ND	2500	2	-
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	4	-
	soil	ND	25.0	4	-
	sludge[c]	8760	8780	4	-
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-
1,2,7,8-TCDF	clay	ND	5.0	4	3.9
	soil	ND	25.0	4	1.0
	sludge	ND	125	4	7.2
	fly ash	7.4	7.4	3	7.6
	still bottom	ND	2500	2	-
1,2,3,7,8-PeCDF	clay	ND	5.0	4	6.1
	soil	ND	25.0	4	5.0
	sludge	ND	125	4	4.8
	fly ash	ND	46	2	-
	still bottom[3]	25600	28100	2	-
1,2,3,4,7,8-HxCDF	clay	ND	5.0	4	26
	soil	ND	25.0	4	6.8
	sludge	13.6	139	4	5.6
	fly ash	24.2	24.2	4	13.5
	still bottom	ND	2500	2	-

TABLE 5. (Continued)

Compound	Matrix[a]	Analyte level (ng/g) Native	Native + spike	N	Percent RSD
OCDF	clay	ND	-	-	-
	soil	ND	-	-	-
	sludge	192	317	4	3.3
	fly ash	ND	-	-	-
	still bottom	ND	-	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri, soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator; resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenolic wastewaters.

Cleanup of clay, soil and fly ash samples was through alumina column only. (Carbon column not used.)

[b]ND - not detected at concentration injected (final volume 0.1 mL or greater).

[c]Estimated concentration out of calibration range of standards.

TABLE 6. RECOVERY DATA FOR REVISED METHOD 8280

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
2,3,7,8-TCDD	clay	ND	5.0	61.7
	soil	378	-	-
	sludge	ND	125	90.0
	fly ash	ND	46	90.0
	still bottom	487	-	-
1,2,3,4-TCDD	clay	ND	5.0	67.0
	soil	ND	25.0	60.3
	sludge	ND	125	73.1
	fly ash	38.5	46	105.6
	still bottom	ND	2500	93.8
1,3,6,8-TCDD	clay	ND	2.5	39.4
	soil	ND	25.0	64.0
	sludge	ND	125	64.5
	fly ash	19.1	46	127.5
	still bottom	227	2500	80.2
1,3,7,9-TCDD	clay	ND	2.5	68.5
	soil	ND	25.0	61.3
	sludge	ND	125	78.4
	fly ash	58.4	46	85.0
	still bottom	ND	2500	91.7
1,3,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	79.3
	sludge	ND	125	78.9
	fly ash	16.0	46	80.2
	still bottom	615	2500	90.5
1,2,7,8-TCDD	clay	ND	5.0	68.0
	soil	ND	25.0	75.3
	sludge	ND	125	80.4
	fly ash	2.6	46	90.4
	still bottom	ND	2500	88.4
1,2,8,9-TCDD	clay	ND	5.0	59.7
	soil	ND	25.0	60.3
	sludge	ND	125	72.8
	fly ash	ND	46	114.3
	still bottom	ND	2500	81.2

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7-PeCDD	clay	ND	5.0	58.4
	soil	ND	25.0	62.2
	sludge	ND	125	79.2
	fly ash	25.8	46	102.4
	still bottom	ND	2500	81.8
1,2,3,7,8-PeCDD	clay	ND	5.0	61.7
	soil	ND	25.0	68.4
	sludge	ND	125	81.5
	fly ash	ND	46	104.9
	still bottom	ND	2500	84.0
1,2,3,4,7,8-HxCDD	clay	ND	5.0	46.8
	soil	ND	25.0	65.0
	sludge	ND	125	81.9
	fly ash	ND	46	125.4
	still bottom	ND	2500	89.1
1,2,3,4,6,7,8-HpCDD	clay	ND	5.0	ND
	soil	ND	25.0	ND
	sludge[d]	8780	125	-
	fly ash	ND	-	-
	still bottom	ND	-	-
2,3,7,8-TCDD (C-13)	clay	ND	5.0	64.9
	soil	ND	25.0	78.8
	sludge	ND	125	78.6
	fly ash	ND	46	88.6
	still bottom	ND	2500	69.7
1,2,7,8-TCDF	clay	ND	5.0	65.4
	soil	ND	25.0	71.1
	sludge	ND	125	80.4
	fly ash	7.4	46	90.4
	still bottom	ND	2500	104.5
1,2,3,7,8-PeCDF	clay	ND	5.0	57.4
	soil	ND	25.0	64.4
	sludge	ND	125	84.8
	fly ash	ND	46	105.8
	still bottom	25600	2500	-

TABLE 6. (Continued)

Compound	Matrix[a]	Native[b] (ng/g)	Spiked[c] level (ng/g)	Mean percent recovery
1,2,3,4,7,8-HxCDF	clay	ND	5.0	54.2
	soil	ND	25.0	68.5
	sludge	13.6	125	82.2
	fly ash	24.2	46	91.0
	still bottom	ND	2500	92.9
OCDF	clay	ND	-	-
	soil	ND	-	-
	sludge	192	125	86.8
	fly ash	ND	-	-
	still bottom	ND	-	-

[a]matrix types:

clay: pottery clay.

soil: Times Beach, Missouri soil blended to form a homogeneous sample. This sample was analyzed as a performance evaluation sample for the Contract Laboratory Program (CLP) in April 1983. The results from EMSL-LV and 8 contract laboratories using the CLP protocol were 305.8 ng/g 2,3,7,8-TCDD with a standard deviation of 81.0.

fly ash: ash from a municipal incinerator: resource recovery ash No. 1.

still bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.

sludge: sludge from cooling tower which received both creosote and pentachlorophenol wastewaters.

The clay, soil and fly ash samples were subjected to alumina column cleanup, no carbon column was used.

[b]Final volume of concentrate 0.1 mL or greater, ND means below quantification limit, 2 or more samples analyzed.

[c]Amount of analyte added to sample, 2 or more samples analyzed.

[d]Estimated concentration out of calibration range of standards.

TABLE 7. LINEAR RANGE AND VARIATIOIN OF RESPONSE FACTORS

Analyte	Linear range tested (pg)	n[b]	Mean RF	%RSD
1,2,7,8-TCDF[a]	50-6000	8	1.634	12.0
2,3,7,8-TCDD[a]	50-7000	7	0.721	11.9
2,3,7,8-TCDF	300-4000	5	2.208	7.9

[a]Response factors for these analytes were calculated using 2,3,7,8-TCDF as the internal standard. The response factors for 2,3,7,8-TCDF were calculated vs. $^{13}C_{12}$-1,2,3,4-TCDD.

[b]Each value of n represents a different concentration level.

TABLE 8. METHOD DETECTION LIMITS OF $^{13}C_{12}$ - LABELED PCDD'S and PCDF'S IN REAGENT WATER (PPT) AND ENVIRONMENTAL SAMPLES (PPB)

$^{13}C_{12}$-Labeled Analyte	Reagent Water[a]	Missouri Soil[b]	Fly-Ash[b]	Industrial Sludge[c]	Still-Bottom[d]	Fuel Oil[d]	Fuel Oil/Sawdust[b]
2,3,7,8-TCDD	0.44	0.17	0.07	0.82	1.81	0.75	0.13
1,2,3,7,8-PeCDD	1.27	0.70	0.25	1.34	2.46	2.09	0.18
1,2,3,6,7,8-HxCDD	2.21	1.25	0.55	2.30	6.21	5.02	0.36
1,2,3,4,6,7,8-HpCDD	2.77	1.87	1.41	4.65	4.59	8.14	0.51
OCDD	3.93	2.35	2.27	6.44	10.1	23.2	1.48
2,3,7,8-TCDF	0.63	0.11	0.06	0.46	0.26	0.48	0.40
1,2,3,7,8-PeCDF	1.64	0.33	0.16	0.92	1.61	0.80	0.43
1,2,3,4,7,8-HxCDF	2.53	0.83	0.30	2.17	2.27	2.09	2.22

[a] Sample size 1,000 mL.
[b] Sample size 10 g.
[c] Sample size 2 g.
[d] Sample size 1 g.
Note: The final sample-extract volume was 100 uL for all samples.

Matrix types used in MDL Study:

- Reagent water: distilled, deionized laboratory water.
- Missouri soil: soil blended to form a homogeneous sample.
- Fly-ash: alkaline ash recovered from the electrostatic precipitator of a coal-burning power plant.
- Industrial sludge: sludge from cooling tower which received creosotic and pentachlorophenolic wastewaters. Sample was ca. 70 percent water, mixed with oil and sludge.
- Still-bottom: distillation bottoms (tar) from 2,4-dichlorophenol production.
- Fuel oil: wood-preservative solution from the modified Thermal Process tanks. Sample was an oily liquid (>90 percent oil) containing no water.
- Fuel oil/Sawdust: sawdust was obtained as a very fine powder from the local lumber yard. Fuel oil (described above) was mixed at the 4 percent (w/w) level.

Procedure used for the Determination of Method Detection Limits was obtained from "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater" Appendix A, EPA-600/4-82-057, July 1982. Using this procedure, the method detection limit is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero.

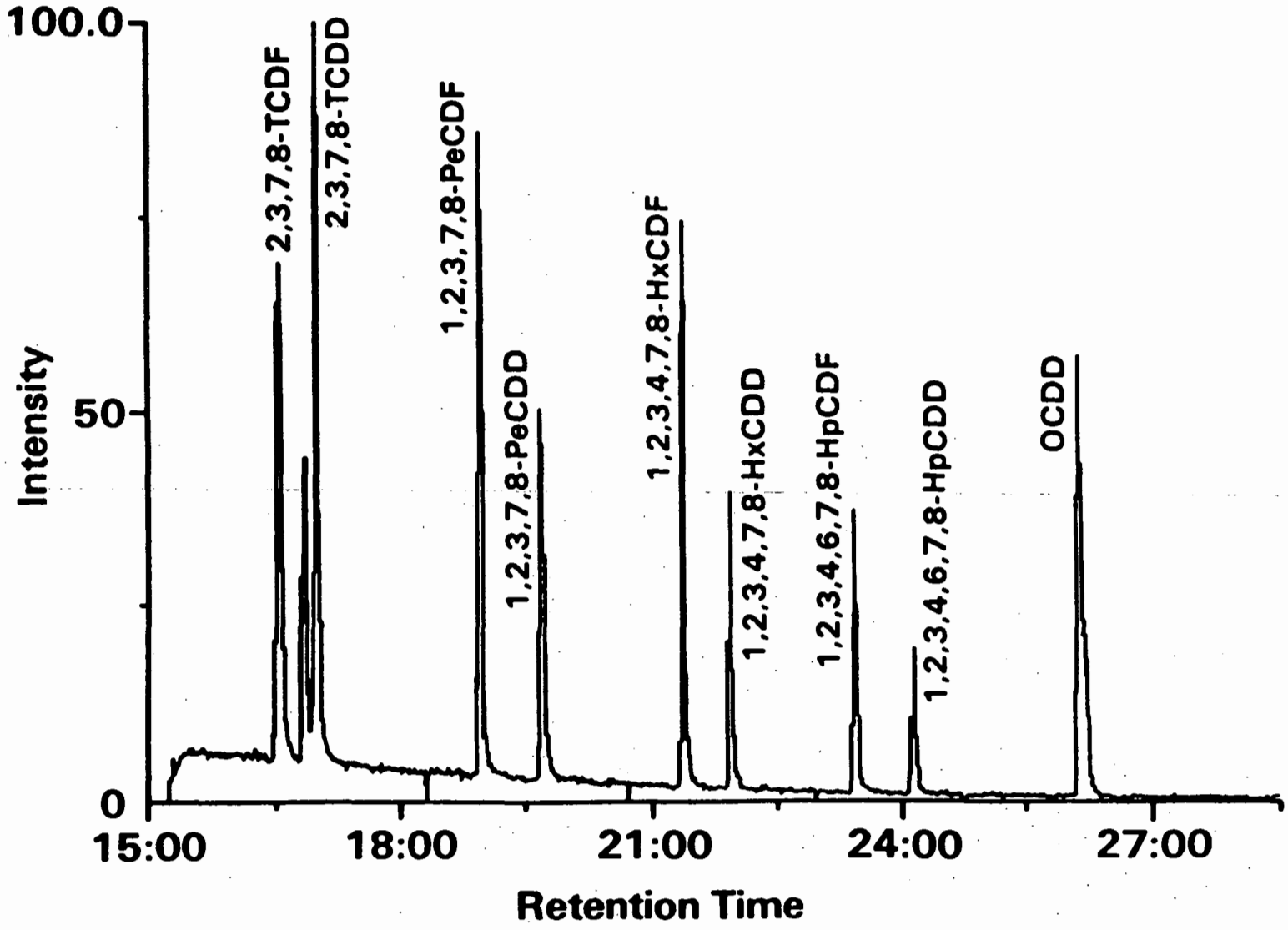
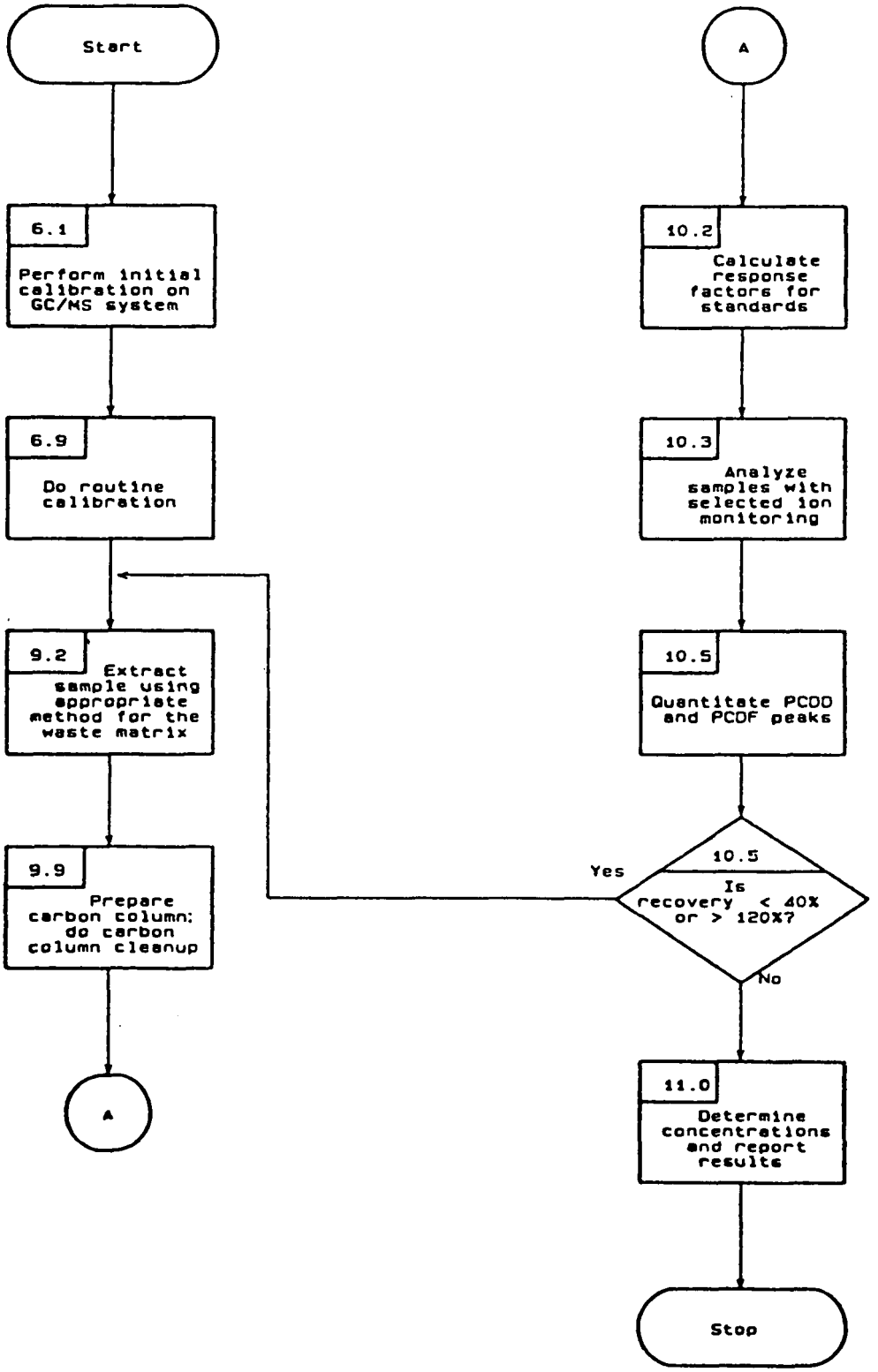


Figure 2. Mass Chromatogram of Selected PCDD and PCDF Congeners.


Start
6.1
Perform initial calibration on GC/MS system
6.9
Do routine calibration
9.2
Extract sample using appropriate method for the waste matrix
9.9
Prepare carbon column; do carbon column cleanup
A
A
10.2
Calculate response factors for standards
10.3
Analyze samples with selected ion monitoring
10.5
Quantitate PCDD and PCDF peaks
10.5
Is recovery < 40% or > 120%?
Yes
No
11.0
Determine concentrations and report results
Stop

APPENDIX A

SIGNAL-TO-NOISE DETERMINATION METHODS

MANUAL DETERMINATION

This method corresponds to a manual determination of the S/N from a GC/MS signal, based on the measurement of its peak height relative to the baseline noise. The procedure is composed of four steps as outlined below. (Refer to Figure 1 for the following discussion).

1. Estimate the peak-to-peak noise (N) by tracing the two lines (E_1 and E_2) defining the noise envelope. The lines should pass through the estimated statistical mean of the positive and the negative peak excursions as shown in Figure 1. In addition, the signal offset (O) should be set high enough such that negative-going noise (except for spurious negative spikes) is recorded.

2. Draw the line (C) corresponding to the mean noise between the segments defining the noise envelope.

3. Measure the height of the GC/MS signal (S) at the apex of the peak relative to the mean noise C. For noisy GC/MS signals, the average peak height should be measured from the estimated mean apex signal D between E_3 and E_4.

4. Compute the S/N.

This method of S/N measurement is a conventional, accepted method of noise measurement in analytical chemistry.

INTERACTIVE COMPUTER GRAPHICAL METHOD

This method calls for the measurement of the GC/MS peak area using the computer data system and Eq. 1:

$$S/N = \frac{A/t}{\frac{A_l/2t + A_r/2t}{2}}$$

where t is the elution time window (time interval, t_2-t_2, at the base of the peak used to measure the peak area A). (Refer to Figure 2, for the following discussion).

A_l and A_r correspond to the areas of the noise level in a region to the left (A_l) and to the right (A_r) of the GC peak of interest.

The procedure to determine the S/N is as follows:

1. Estimate the average negative peak excursions of the noise (i.e., the low segment-E_2-of the noise envelope). Line E_2 should pass through the estimated statistical mean of the negative-going noise excursions. As stated earlier, it is important to have the signal offset (0) set high enough such that negative-going noise is recorded.

2. Using the cross-hairs of the video display terminal, measure the peak area (A) above a baseline corresponding to the mean negative noise value (E_2) and between the time t_1 and t_2 where the GC/MS peak intersects the baseline, E_2. Make note of the time width $t=t_2-t_1$.

3. Following a similar procedure as described above, measure the area of the noise in a region to the left (A_l) and to the right (A_r) of the GC/MS signal using a time window twice the size of t, that is, 2 x t.

The analyst must sound judgement in regard to the proper selection of interference-free regions in the measurement of A_l and A_r. It is not recommended to perform these noise measurements (A_l and A_r) in remote regions exceeding ten time widths (10t).

4. Compute the S/N using Eq. 1.

NOTE: If the noise does not occupy at least 10 percent of the vertical axis (i.e., the noise envelope cannot be defined accurately), then it is necessary to amplify the vertical axis so that the noise occupies 20 percent of the terminal display (see Figure 3).

FIGURE CAPTIONS

Figure 1. Manual determination of S/N.
The peak height (S) is measured between the mean noise (lines C and D). These mean signal values are obtained by tracing the line between the baseline average noise extremes, E_1 and E_2, and between the apex average noise extremes, E_3 and E_4, at the apex of the signal. Note, it is imperative that the instrument's interface amplifier electronic's zero offset be set high enough such that negative-going baseline noise is recorded.

Figure 2. Interactive determination of S/N.
The peak area (A) is measured above the baseline average negative noise E_2 and between times t_1 and t_2. The noise is obtained from the areas A_1 and A_r measured to the left and to the right of the peak of interest using time windows T_1 and T_r (T_1=T_r=2t).

Figure 3. Interactive determination of S/N.
A) Area measurements without amplification of the vertical axis. Note that the noise cannot be determined accurately by visual means. B) Area measurements after amplification (10X) of the vertical axis so that the noise level occupies approximately 20 percent of the display, thus enabling a better visual estimation of the baseline noise, E_1, E_2, and C.

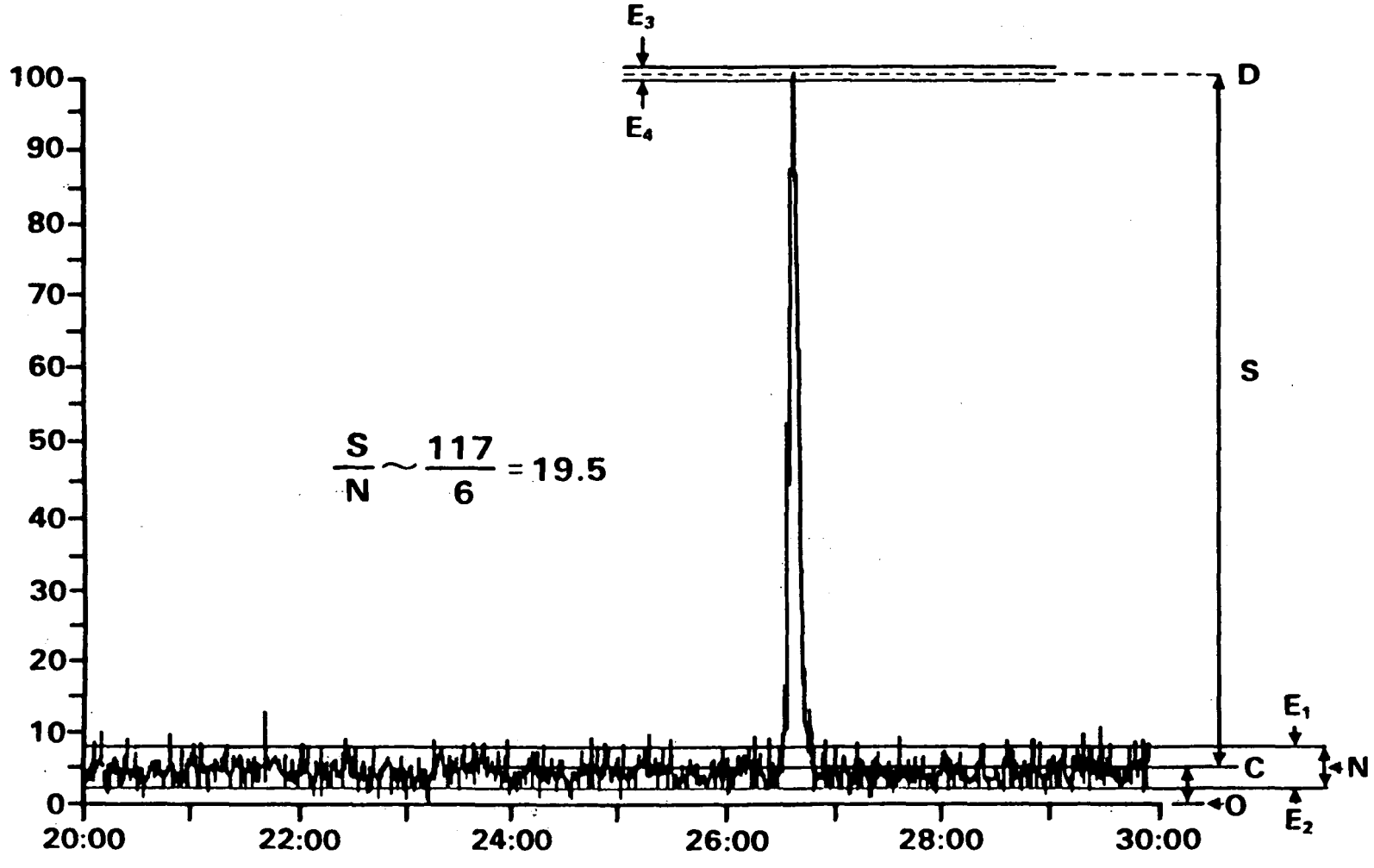


Figure 1. Manual Determination of S/N.

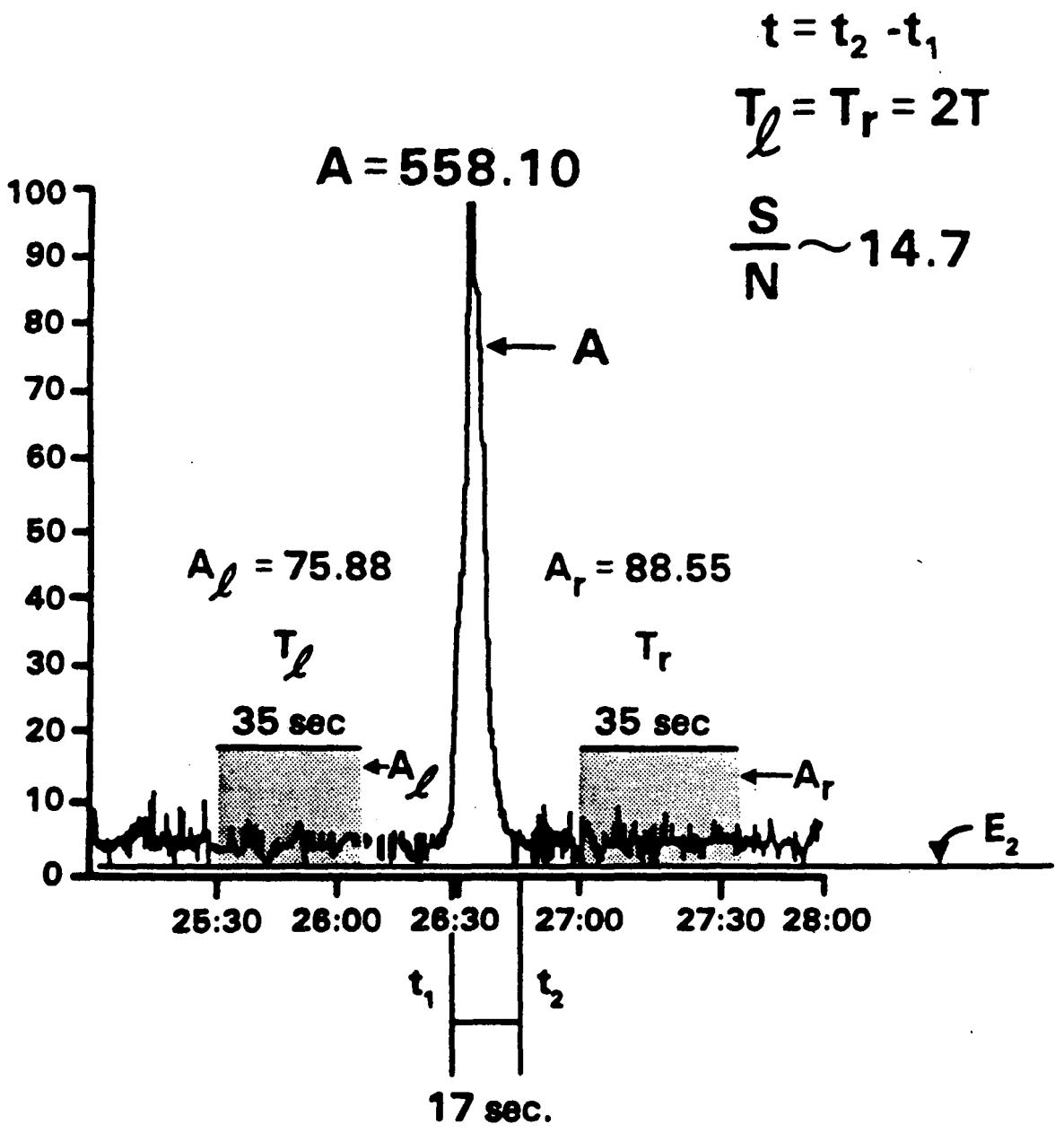


Figure 2. Interactive Determination of S/N.

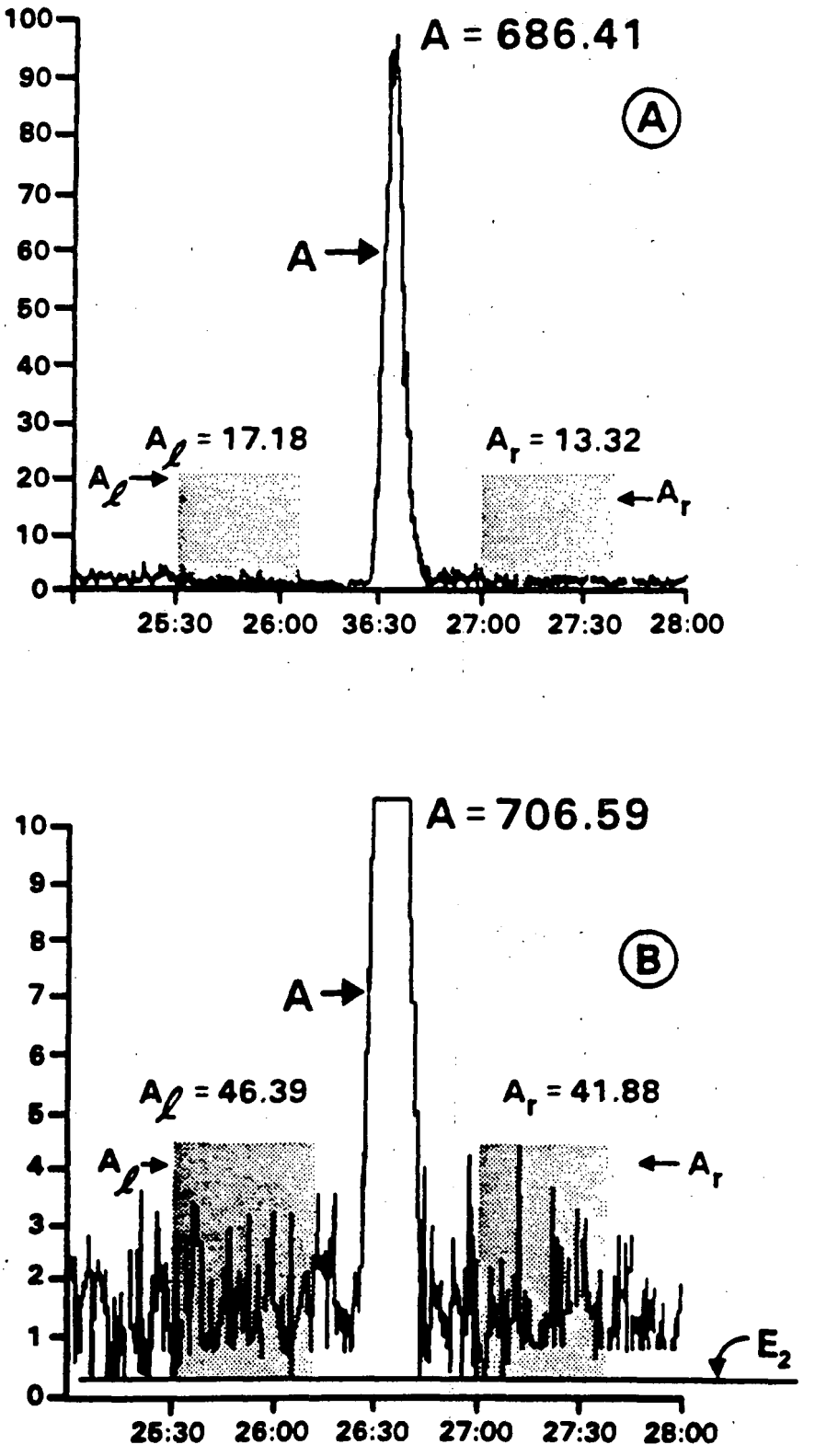


Figure 3. Interactive Determination of S/N.

APPENDIX B

RECOMMENDED SAFETY AND HANDLING PROCEDURES FOR PCDD'S/PCDF'S

1. The human toxicology of PCDD/PCDF is not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 perent to 0.14 percent. The physical properties of the 135 other tetra- through octa-chlorinated PCDD/PCDF have not been well established, although it is presumed that the physical properties of these congeners are generally similar to those of the 2,3,7,8-TCDD isomer. On the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks.

2. PCDD/PCDF and samples containing these are handled using essentially the same techniques as those employed in handling radioactive or infectious materials. Well-ventilated, controlled-access laboratories are required, and laboratory personel entering these laboratories should wear appropriate safety clothing, including disposable coveralls, shoe covers, gloves, and face and head masks. During analytical operations which may give rise to aerosols or dusts, personnel should wear respirators equipped with activated carbon filters. Eye protection equipment (preferably full face shields) must be worn at all times while working in the analytical laboratory with PCDD/PCDF. Various types of gloves can be used by personnel, depending upon the analytical operation being accomplished. Latex gloves are generally utilized, and when handling samples thought to be particularly hazardous, an additional set of gloves are also worn beneath the latex gloves (for example, Playtex gloves supplied by American Scientific Products, Cat. No. 67216). Bench-tops and other work surfaces in the laboratory should be covered with plastic-backed absorbent paper during all analytical processing. When finely divided samples (dusts, soils, dry chemicals) are processed, removal of these from sample contaners, as well as other operations, including weighing, transferring, and mixing with solvents, should all be accomplished within a glove box. Glove boxes, hoods and the effluents from mechanical vacuum pumps and gas chromatographs on the mass spectrometers should be vented to the atmosphere preferably only after passing through HEPA particulate filters and vapor-sorbing charcoal.

3. All laboratory ware, safety clothing, and other items potentially contaminated with PCDD/PCDF in the course of analyses must be carefully secured and subjected to proper disposal. When feasible, liquid wastes are concentrated, and the residues are placed in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Glass and combustible items are compacted using a dedicated trash compactor used only for hazardous waste materials and then placed in the same type of disposal drum. Disposal of accumulated wastes is periodically accomplished by high temperature incineration at EPA-aproved facilities.

4. Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the laboratory. Typically, if the detectable level of TCDD or TCDF from such a test is greater than 50 ng/m^2, this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/m^2. In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

5. In the unlikely event that analytical personnel experience skin contact with PCDD/PCDF or samples containing these, the contaminated skin area should immediately be thoroughly scurbbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.

6. It is desirable that personnel working in laboratories where PCDD/PCDF are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based upon published clinical observations, are appropriate for persons who may be exposed to PCDD/PCDF. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No._____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

Revision 0
Date September 1986

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ng/g)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

Revision 0
Date September 1986

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDD	PeCDD	HxCDD	HpCDD	OCDD

DATA RELEASE AUTHORIZED BY _____

DIOXIN SAMPLE DATA SUMMARY FORM 8280-1-W

LAB NAME _____ CONTRACT No. _____

CASE No. _____

QUANTITY FOUND (ug/L)

SAMPLE NO.	FILE NAME	TCDF	PeCDF	HxCDF	HpCDF	OCDF

DIOXIN RAW SAMPLE DATA FORM 8280-2

LAB NAME _____ ANALYST(s) _____ CASE No. _____

SAMPLE No. _____ TYPE OF SAMPLE _____ CONTRACT No. _____

SAMPLE SIZE _____ % MOISTURE _____ FINAL EXTRACT VOLUME _____

EXTRACTION METHOD _____ ALIQUOT USED FOR ANALYSIS _____

CLEAN UP OPTION _____

CONCENTRATION FACTOR _____ DILUTION FACTOR _____

DATE EXTRACTED _____ DATA ANALYZED _____

VOLUME $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____ TO SAMPLE VOLUME _____

VOLUME INJECTED _____ Wt $^{13}C_{12}$-1,2,3,4-TCDD ADDED _____

Wt $^{13}C_{12}$-2,3,7,8-TCDD ADDED _____ $^{13}C_{12}$-2,3,7,8-TCDD % RECOVERY _____

Wt $^{13}C_{12}$-2,3,7,8-OCDD ADDED _____ $^{13}C^{12}$-OCDD % RECOVERY _____

$^{13}C_{12}$-2,3,7,8-TCDD RRF _____ $^{13}C_{12}$-OCDD RRF _____

$^{13}C_{12}$-2,3,7,8-TCDD

AREA 332 _____ AREA 334 _____ RATIO 332/334 _____

$^{13}C_{12}$-OCDD AREA 470 _____ AREA 472 _____ RATIO 470/472 _____

RT 2,3,7,8-TCDD (Standard) _____ RT 2,3,7,8-TCDD (Sample) _____

$^{13}C_{12}$-2,3,7,8-TCDD - $^{13}C_{12}$-1,2,3,4-TCDD Percent Valley _____

Revision 0
Date September 1986

DIOXIN INITIAL CALIBRATION STANDARD DATA SUMMARY

FORM 8280-3

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s)_____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD_____ or $^{13}C_{12}$-1,2,3,^{4}-TCDD_____

CALIBRATION STANDARD	RRF 1	RRF 2	RRF 3	RRF 4	RRF 5	MEAN	%RSD
TCDD							
PeCDD							
HxCDD							
HpCDD							
OCDD							
TCDF							
PeCDF							
HxCDF							
HpCDF							
OCDF							

FORM 8280-3 (Continued)

CONCENTRATIONS IN PG/UL

	1	2	3	4	5
TCDD					
PeCDD					
HxCDD					
HpCDD					
OCDD					
TCDF					
PeCDF					
HxCDF					
HpCDF					
OCDF					

DIOXIN CONTINUING CALIBRATION SUMMARY

FORM 8280-4

CASE No. _____

Lab Name _____ Contract No. _____

Date of Initial Calibration _____ Analyst(s) _____

Relative to $^{13}C_{12}$-2,3,7,8-TCDD _____ or $^{13}C_{12}$-1,2,3,4-TCDD _____

COMPOUND	$\overline{RRF}$	RRF	%D
TCDD			
PeCDD			
HxCDD			
HpCDD			
OCDD			
TCDF			
PeCDF			
HxCDF			
HpCDF			
OCDF			

Revision 0
Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-A

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

TCDD REQUIRED 320/322 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 322	AREA 320	AREA 257	320/ 322	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

TCDF REQUIRED 304/306 RATIO WINDOW IS 0.65 - 0.89

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 306	AREA 304	AREA 243	304/ 306	CONFIRM AS TCDD Y/N	CONC.

TOTAL TCDD _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-B

LAB NAME _____ ANALYST(s) _____ CASE No. _____

CONTRACT No. _____ SAMPLE No. _____

PeCDD REQUIRED 320/322 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 356	AREA 358	AREA 354	AREA 293	358/ 356	CONFIRM AS PeCDD Y/N	CONC.

TOTAL PeCDD _____

PeCDF REQUIRED 342/340 RATIO WINDOW IS 0.55 - 0.75

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 340	AREA 342	AREA 338	AREA 277	342/ 340	CONFIRM AS PeCDF Y/N	CONC.

TOTAL PeCDF _____

Revision 0
Date September 1986

DIOXIN RAW SAMPLE DATA FORM 8280-5-C

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HxCDD REQUIRED 392/390 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 390	AREA 392	AREA 388	AREA 327	392/ 390	CONFIRM AS HxCDD Y/N	CONC.

TOTAL HxCDD _____

HxCDF REQUIRED 376/374 RATIO WINDOW IS 0.69 - 0.93

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 376	AREA 374	AREA 372	AREA 311	376/ 374	CONFIRM AS HxCDF Y/N	CONC.

TOTAL HxCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-D

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No._____ SAMPLE No._____

HpCDD REQUIRED 426/444 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 424	AREA 426	AREA 422	AREA 361	426/ 424	CONFIRM AS HpCDD Y/N	CONC.

TOTAL HpCDD _____

HpCDF REQUIRED 410/408 RATIO WINDOW IS 0.83 - 1.12

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 408	AREA 410	AREA 406	AREA 345	410/ 408	CONFIRM AS HpCDF Y/N	CONC.

TOTAL HpCDF _____

DIOXIN RAW SAMPLE DATA FORM 8280-5-E

LAB NAME _____ ANALYST(s) _____ CASE No._____

CONTRACT No. _____ SAMPLE No. _____

OCDD REQUIRED 458/460 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 460	AREA 458	AREA 395	458/ 460	CONFIRM AS OCDD Y/N	CONC.

TOTAL OCDD _____

OCDF REQUIRED 442/444 RATIO WINDOW IS 0.75 - 1.01

QUANTITATED FROM 2,3,7,8-TCDD _____ 1,2,3,4-TCDD _____ RRF _____

SCAN #	RRT	AREA 444	AREA 442	AREA 379	442/ 444	CONFIRM AS OCDF Y/N	CONC.

TOTAL OCDF _____

DIOXIN SYSTEM PERFORMANCE CHECK ANALYSIS FORM 8280-6

LAB NAME _____ CASE No. _____

BEGINNING DATE _____ TIME _____ CONTRACT No._____

ENDING DATE _____ TIME _____ ANALYST(s) _____

PC SOLUTION IDENTIFIER _____

ISOTOPIC RATIO CRITERIA MEASUREMENT

PCDD's	IONS RATIOED	RATIO AT BEGINNING OF 12 HOUR PERIOD	RATIO AT END OF 12 HOUR PERIOD	ACCEPTABLE WINDOW
Tetra	320/322			0.65-0.89
Penta	358/356			0.55-0.75
Hexa	392/390			0.69-0.93
Hepta	426/424			0.83-1.12
Octa	458/460			0.75-1.01
PCDF's				
Tetra	304/306			0.65-0.89
Penta	342-340			0.55-0.75
Hexa	376-374			0.69-0.93
Hepta	410/408			0.83-1.12
Octa	442/444			0.75-1.01

Ratios out of criteria

	Beginning	End
PCDD	_____ out of _____	_____ out of _____
PCDF	_____ out of _____	_____ out of _____

NOTE: One form is required for each 12 hour period samples are analyzed.

METHOD 8310

POLYNUCLEAR AROMATIC HYDROCARBONS

1.0 SCOPE AND APPLICATION

1.1 Method 8310 is used to determine the concentration of certain polynuclear aromatic hydrocarbons (PAH) in ground water and wastes. Specifically, Method 8310 is used to detect the following substances:

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

1.2 Use of Method 8310 presupposes a high expectation of finding the specific compounds of interest. If the user is attempting to screen samples for any or all of the compounds listed above, he must develop independent protocols for the verification of identity.

1.3 The method detection limits for each compound in reagent water are listed in Table 1. Table 2 lists the practical quantitation limit (PQL) for other matrices. The sensitivity of this method usually depends on the level of interferences rather than instrumental limitations. The limits of detection listed in Table 1 for the liquid chromatographic approach represent sensitivities that can be achieved in the absence of interferences. When interferences are present, the level of sensitivity will be lower.

1.4 This method is recommended for use only by experienced residue analysts or under the close supervision of such qualified persons.

2.0 SUMMARY OF METHOD

2.1 Method 8310 provides high performance liquid chromatographic (HPLC) conditions for the detection of ppb levels of certain polynuclear aromatic hydrocarbons. Prior to use of this method, appropriate sample extraction techniques must be used. A 5- to 25-uL aliquot of the extract is injected into an HPLC, and compounds in the effluent are detected by ultraviolet (UV) and fluorescence detectors.

2.2 If interferences prevent proper detection of the analytes of interest, the method may also be performed on extracts that have undergone cleanup using silica gel column cleanup (Method 3630).

TABLE 1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF PAHs[a]

Compound	Retention time (min)	Column capacity factor (k')	Method Detection limit (ug/L)	
			UV	Fluorescence
Naphthalene	16.6	12.2	1.8	
Acenaphthylene	18.5	13.7	2.3	
Acenaphthene	20.5	15.2	1.8	
Fluorene	21.2	15.8	0.21	
Phenanthrene	22.1	16.6		0.64
Anthracene	23.4	17.6		0.66
Fluoranthrene	24.5	18.5		0.21
Pyrene	25.4	19.1		0.27
Benzo(a)anthracene	28.5	21.6		0.013
Chrysene	29.3	22.2		0.15
Benzo(b)fluoranthene	31.6	24.0		0.018
Benzo(k)fluoranthene	32.9	25.1		0.017
Benzo(a)pyrene	33.9	25.9		0.023
Dibenzo(a,h)anthracene	35.7	27.4		0.030
Benzo(ghi)perylene	36.3	27.8		0.076
Indeno(1,2,3-cd)pyrene	37.4	28.7		0.043

[a] HPLC conditions: Reverse phase HC-ODS Sil-X, 5 micron particle size, in a 250-mm x 2.6-mm I.D. stainless steel column. Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

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

[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.

3.0 INTERFERENCES

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

3.2 Interferences coextracted from the samples will vary considerably from source to source. Although a general cleanup technique is provided as part of this method, individual samples may require additional cleanup approaches to achieve the sensitivities stated in Table 1.

3.3 The chromatographic conditions described allow for a unique resolution of the specific PAH compounds covered by this method. Other PAH compounds, in addition to matrix artifacts, may interfere.

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). Ground-glass stopper is used to prevent evaporation of extracts.

4.1.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 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: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.3 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.4 Syringe: 5-mL.

4.5 High pressure syringes.

4.6 HPLC apparatus:

4.6.1 **Gradient pumping system:** Constant flow.

4.6.2 **Reverse phase column:** HC-ODS Sil-X, 5-micron particle size diameter, in a 250-mm x 2.6-mm I.D. stainless steel column (Perkin Elmer No. 089-0716 or equivalent).

4.6.3 **Detectors:** Fluorescence and/or UV detectors may be used.

4.6.3.1 Fluorescence detector: For excitation at 280-nm and emission greater than 389-nm cutoff (Corning 3-75 or equivalent). Fluorometers should have dispersive optics for excitation and can utilize either filter or dispersive optics at the emission detector.

4.6.3.2 UV detector: 254-nm, coupled to the fluorescence detector.

4.6.4 **Strip-chart recorder:** compatible with detectors. A data system for measuring peak areas and retention times is recommended.

4.7 Volumetric flasks: 10-, 50-, and 100-mL.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as water in which an interferent is not observed at the method detection limit of the compounds of interest.

5.2 Acetonitrile: HPLC quality, distilled in glass.

5.3 Stock standard solutions:

5.3.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in acetonitrile 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.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. 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.

5.3.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.4 Calibration standards: Calibration standards at a minimum of five concentration levels should be prepared through dilution of the stock standards with acetonitrile. 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 HPLC. Calibration standards must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.5 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.

5.5.1 Prepare calibration standards at a minimum of five concentration levels for each analyte as described in Paragraph 5.4.

5.5.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with acetonitrile.

5.5.3 Analyze each calibration standard according to Section 7.0.

5.6 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 reagent water blank with one or two surrogates (e.g., decafluorobiphenyl or other PAHs not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for HPLC analysis due to coelution problems.

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 must be 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 pH with methylene chloride, using either Method 3510 or 3520. Solid samples are extracted using either Method 3540 or 3550. To achieve maximum sensitivity with this method, the extract must be concentrated to 1 mL.

7.1.2 Prior to HPLC analysis, the extraction solvent must be exchanged to acetonitrile. 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 95-100°C. Momentarily remove the Snyder column, add 4 mL of acetonitrile, a new boiling chip, and attach a two-ball micro-Snyder column. Concentrate the extract using 1 mL of acetonitrile 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 15-20 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 When the apparatus is cool, remove the micro-Snyder column and rinse its lower joint into the concentrator tube with about 0.2 mL of acetonitrile. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 1.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with HPLC analysis if further cleanup is not required.

7.2 HPLC conditions (Recommended):

7.2.1 Using the column described in Paragraph 4.6.2: Isocratic elution for 5 min using acetonitrile/water (4:6)(v/v), then linear gradient elution to 100% acetonitrile over 25 min at 0.5 mL/min flow rate. If columns having other internal diameters are used, the flow rate should be adjusted to maintain a linear velocity of 2 mm/sec.

7.3 Calibration:

7.3.1 Refer to Method 8000 for proper calibration procedures. The procedure of internal or external standard calibration may be used. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.2 Assemble the necessary HPLC apparatus and establish operating parameters equivalent to those indicated in Section 7.2.1. By injecting calibration standards, establish the sensitivity limit of the detectors and the linear range of the analytical systems for each compound.

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

7.4 HPLC analysis:

7.4.1 Table 1 summarizes the estimate retention times of PAHs determinable by this method. Figure 1 is an example of the separation achievable using the conditions given in Paragraph 7.2.1.

Column: HC-ODS SIL-X
Mobile Phase: 40% to 100% Acetonitrile in Water
Dectector: Fluorescence

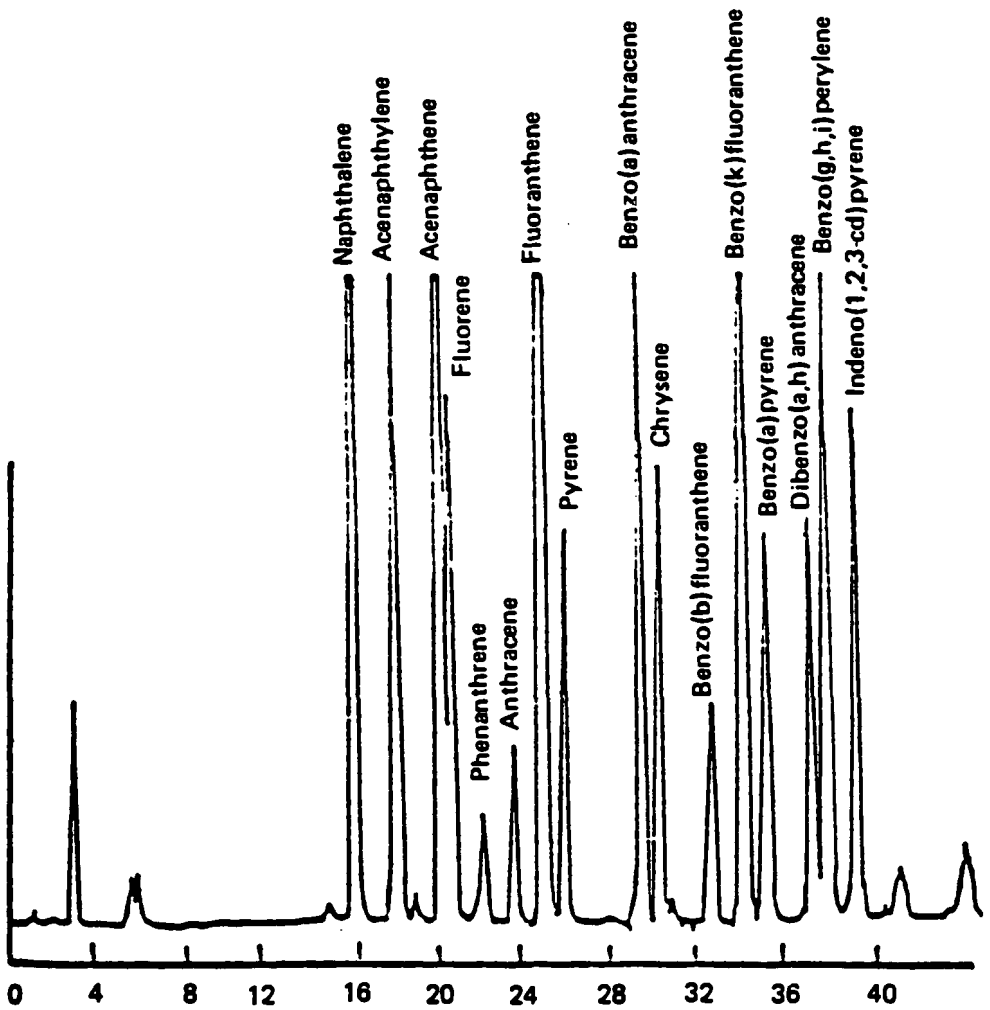


Figure 1. Liquid chromatogram of polynuclear aromatics.

7.4.2 If internal standard calibration is to be performed, add 10 uL of internal standard to the sample prior to injection. Inject 2-5 uL of the sample extract with a high-pressure syringe or sample injection loop. Record the volume injected to the nearest 0.1 uL, and the resulting peak size, in area units or peak heights. Re-equilibrate the HPLC column at the initial gradient conditions for at least 10 min between injections.

7.4.3 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 Section 7.8 of Method 8000 for calculation equations.

7.4.4 If the peak area exceeds the linear range of the system, dilute the extract and reanalyze.

7.4.5 If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

7.5 Cleanup:

7.5.1 Cleanup of the acetonitrile extract takes place using Method 3630 (Silica Gel Cleanup). Specific instructions for cleanup of the extract for PAHs is given in Section 7.1 of Method 3630.

7.5.2 Following cleanup, analyze the samples using HPLC as described in Section 7.4.

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 Mandatory quality control to validate the HPLC system operation is found in Method 8000, Section 8.6.

8.2.1 The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte at the following concentrations in acetonitrile: naphthalene, 100 ug/mL; acenaphthylene, 100 ug/mL; acenaphthene, 100 ug/mL; fluorene, 100 ug/mL; phenanthrene, 100 ug/mL; anthracene, 100 ug/mL; benzo(k)fluoranthene, 5 ug/mL; and any other PAH at 10 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, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are 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 16 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations over the range 0.1 to 425 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 are presented in Table 4.

9.2 This method has been tested for linearity of spike recovery from reagent water and has been demonstrated to be applicable over the concentration range from 8 x MDL to 800 x MDL with the following exception: benzo(ghi)perylene recovery at 80 x and 800 x MDL were low (35% and 45%, respectively).

9.3 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, and calibration procedures used.

10.0 REFERENCES

1. "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 9 - PAHs," Report for EPA Contract 68-03-2624 (in preparation).

2. Sauter, A.D., L.D. Betowski, T.R. Smith, V.A. Strickler, R.G. Beimer, B.N. Colby, and J.E. Wilkinson, "Fused Silica Capillary Column GC/MS for the Analysis of Priority Pollutants," Journal of HRC&CC 4, 366-384, 1981.

3. "Determination of Polynuclear Aromatic Hydrocarbons in Industrial and Municipal Wastewaters," EPA-600/4-82-025, U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268, September 1982.

4. Burke, J.A. "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

5. "EPA Method Validation Study 20, Method 610 (Polynuclear Aromatic Hydrocarbons)," Report for EPA Contract 68-03-2624 (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.

7. Provost, L.P. and R.S. Elder, "Interpretation of Percent Recovery Data," American Laboratory, 15, pp. 58-63, 1983.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range p, p_s (%)
Acenaphthene	100	40.3	D-105.7	D-124
Acenaphthylene	100	45.1	22.1-112.1	D-139
Anthracene	100	28.7	11.2-112.3	D-126
Benzo(a)anthracene	10	4.0	3.1-11.6	12-135
Benzo(a)pyrene	10	4.0	0.2-11.0	D-128
Benzo(b)fluoranthene	10	3.1	1.8-13.8	6-150
Benzo(ghi)perylene	10	2.3	D-10.7	D-116
Benzo(k)fluoranthene	5	2.5	D-7.0	D-159
Chrysene	10	4.2	D-17.5	D-199
Dibenzo(a,h)anthracene	10	2.0	0.3-10.0	D-110
Fluoranthene	10	3.0	2.7-11.1	14-123
Fluorene	100	43.0	D-119	D-142
Indeno(1,2,3-cd)pyrene	10	3.0	1.2-10.0	D-116
Naphthalene	100	40.7	21.5-100.0	D-122
Phenanthrene	100	37.7	8.4-133.7	D-155
Pyrene	10	3.4	1.4-12.1	D-140

s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

p, p_s = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 610. These criteria are based directly upon the method performance data in Table 3. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 3.

TABLE 4. 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)
Acenaphthene	0.52C+0.54	0.39$\bar{X}$+0.76	0.53$\bar{X}$+1.32
Acenaphthylene	0.69C-1.89	0.36$\bar{X}$+0.29	0.42$\bar{X}$+0.52
Anthracene	0.63C-1.26	0.23$\bar{X}$+1.16	0.41$\bar{X}$+0.45
Benzo(a)anthracene	0.73C+0.05	0.28$\bar{X}$+0.04	0.34$\bar{X}$+0.02
Benzo(a)pyrene	0.56C+0.01	0.38$\bar{X}$-0.01	0.53$\bar{X}$-0.01
Benzo(b)fluoranthene	0.78C+0.01	0.21$\bar{X}$+0.01	0.38$\bar{X}$-0.00
Benzo(ghi)perylene	0.44C+0.30	0.25$\bar{X}$+0.04	0.58$\bar{X}$+0.10
Benzo(k)fluoranthene	0.59C+0.00	0.44$\bar{X}$-0.00	0.69$\bar{X}$+0.10
Chrysene	0.77C-0.18	0.32$\bar{X}$-0.18	0.66$\bar{X}$-0.22
Dibenzo(a,h)anthracene	0.41C-0.11	0.24$\bar{X}$+0.02	0.45$\bar{X}$+0.03
Fluoranthene	0.68C+0.07	0.22$\bar{X}$+0.06	0.32$\bar{X}$+0.03
Fluorene	0.56C-0.52	0.44$\bar{X}$-1.12	0.63$\bar{X}$-0.65
Indeno(1,2,3-cd)pyrene	0.54C+0.06	0.29$\bar{X}$+0.02	0.42$\bar{X}$+0.01
Naphthalene	0.57C-0.70	0.39$\bar{X}$-0.18	0.41$\bar{X}$+0.74
Phenanthrene	0.72C-0.95	0.29$\bar{X}$+0.05	0.47$\bar{X}$-0.25
Pyrene	0.69C-0.12	0.25$\bar{X}$+0.14	0.42$\bar{X}$-0.00

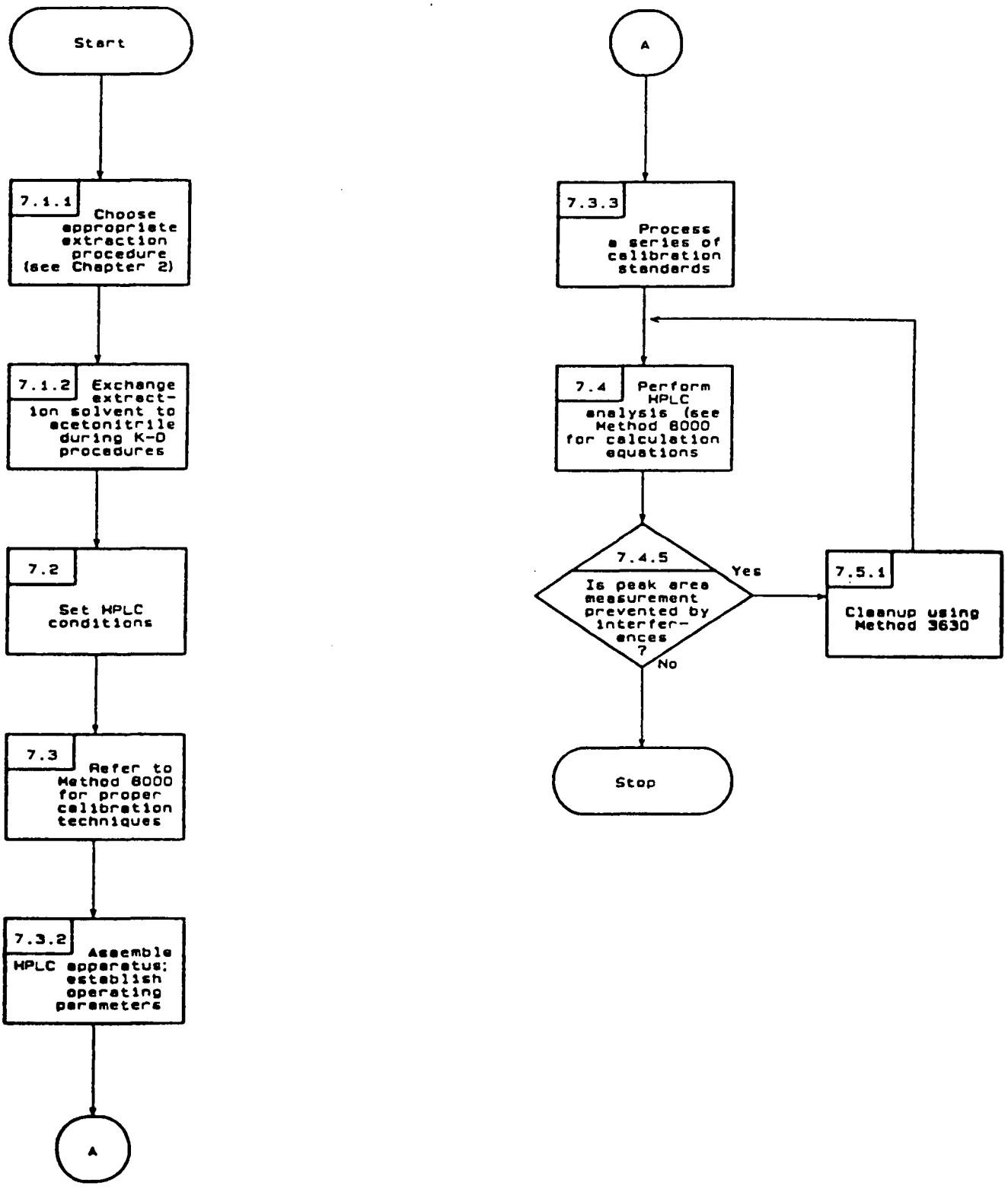
x' = Expected recovery for one or more measurements of a sample containing a concentration of C, in ug/L.

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.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to acetonitrile during K-D procedures
7.2 Set HPLC conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Assemble HPLC apparatus; establish operating parameters
A
A
7.3.3 Process a series of calibration standards
7.4 Perform HPLC analysis (see Method 8000 for calculation equations
7.4.5 Is peak area measurement prevented by interferences ?
Yes
No
7.5.1 Cleanup using Method 3630
Stop

4.4 MISCELLANEOUS SCREENING METHODS

METHOD 3810

HEADSPACE

1.0 SCOPE AND APPLICATION

1.1 Method 3810 was formerly Method 5020 in the second edition of this manual.

1.2 Method 3810 is a static headspace technique for extracting volatile organic compounds from samples. It is a simple method that allows large numbers of samples to be screened in a relatively short period of time. It is ideal for screening samples prior to using the purge-and-trap method. Detection limits for this method may vary widely among samples because of the large variability and complicated matrices of waste samples. The method works best for compounds with boiling points of less than 125°C. The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

1.3 Due to the variability of this method, this procedure is recommended for use only as a screening procedure for other, more accurate determinative methods (Methods 8010, 8015, 8020, 8030, and 8240).

2.0 SUMMARY OF METHOD

2.1 The sample is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas-tight syringe for screening analysis using the conditions specified in one of the GC or GC/MS determinative methods (8010, 8015, 8020, 8030, or 8240).

3.0 INTERFERENCES

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

3.2 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with reagent water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of reagent water. It may be necessary to wash out the syringe with detergent, rinse with distilled water, and dry in a 105°C oven between analyses.

3.3 Before processing any samples, the analyst should demonstrate daily through the analysis of an organic-free water or solvent blank that the entire analytical system is interference-free.

4.0 APPARATUS AND MATERIALS

4.1 Refer to the specific determinative method for appropriate apparatus and materials.

4.2 Vials: 125-mL Hypo-Vials (Pierce Chemical Co., #12995, or equivalent), four each.

4.3 Septa: Tuf-Bond (Pierce #12720 or equivalent).

4.4 Seals: Aluminum (Pierce #13214l or equivalent).

4.5 Crimper: Hand (Pierce #13212 or equivalent).

4.6 Syringe: 5-mL, gas-tight with shutoff valve and chromatographic needles.

4.7 Microsyringe: 250- or 500-uL.

4.8 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

5.0 REAGENTS

5.1 Refer to the specific determinative method and Method 8000 for preparation of calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Section 4.1.

7.0 PROCEDURE

7.1 Gas chromatographic conditions and Calibration: Refer to the specific determinative method for GC operating conditions and to Method 8000, Section 7.4, for calibration procedures.

7.2 Sample preparation:

7.2.1 Place 10.0 g of a well-mixed waste sample into each of two separate 125-mL septum-seal vials.

7.2.2 Dose one sample vial through the septum with 200 uL of a 50 ng/uL calibration standard containing the compounds of interest. Label this "1-ppm spike."

7.2.3 Dose a separate (empty) 125-mL septum seal vial with 200 uL of the same 50 ng/uL calibration standard. Label this "1-ppm standard."

7.2.4 Place the sample, 1-ppm-spike, and 1-ppm-standard vials into a 90°C water bath for 1 hr. Store the remaining sample vial at 4.0°C for possible future analysis.

7.3 Sample analysis:

7.3.1 While maintaining the vials at 90°C, withdraw 2 mL of the headspace gas with a gas-tight syringe and analyze by direct injection into a GC. The GC should be operated using the same GC conditions listed in the method being screened (8010, 8015, 8020, 8030, or 8240).

7.3.2 Analyze the 1-ppm standard and adjust instrument sensitivity to give a minimum response of at least 2 times the background. Record retention times (RT) and peak areas of compounds of interest.

7.3.3 Analyze the 1-ppm spiked sample in the same manner. Record RTs and peak areas.

7.3.4 Analyze the undosed sample as in Paragraph 7.3.3.

7.3.5 Use the results obtained to determine if the sample requires dilution or methanolic extraction as indicated in Method 5030.

8.0 QUALITY CONTROL

8.1 Before processing any samples, the analyst should demonstrate through the analysis of a distilled water method blank that all glassware and reagents are interference-free. Each time a set of samples is extracted or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.2 Standard quality assurance practices should be used with this method. Fortified samples should be carried through all stages of sample preparation and measurement; they should be analyzed to validate the sensitivity and accuracy of the analysis. If the fortified waste samples do not indicate sufficient sensitivity to detect less than or equal to 1 ug/g of sample, then the sensitivity of the instrument should be increased.

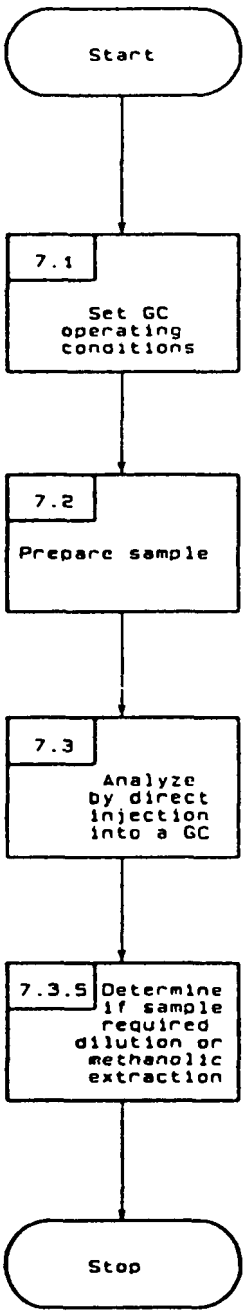
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Hachenberg, H. and A. Schmidt, Gas Chromatographic Headspace Analysis, Philadelphia: Hayden & Sons Inc., 1979.

2. Friant, S.L. and I.H. Suffet, "Interactive Effects of Temperature, Salt Concentration and pH on Headspace Analysis for Isolating Volatile Trace Organics in Aqueous Environmental Samples," Anal. Chem. 51, 2167-2172, 1979.


Start
7.1
Set GC operating conditions
7.2
Prepare sample
7.3
Analyze by direct injection into a GC
7.3.5
Determine if sample required dilution or methanolic extraction
Stop

METHOD 3820

HEXADECANE EXTRACTION AND SCREENING OF PURGEABLE ORGANICS

1.0 SCOPE AND APPLICATION

1.1 This method is a screening procedure for use with purge-and-trap GC or GC/MS. The results of this analysis are purely qualitative and should not be used as an alternative to more detailed and accurate quantitation methods.

2.0 SUMMARY OF METHOD

2.1 An aliquot of sample is extracted with hexadecane and then analyzed by GC/FID. The results of this analysis will indicate whether the sample requires dilution or methanolic extraction prior to purge-and-trap GC or GC/MS analysis.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants in solvents, reagents, and glassware. All these materials must be routinely demonstrated to be free from contaminants by running laboratory reagent blanks. Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from sample to sample depending upon the nature and diversity of the water being sampled.

3.2 The flame ionization detector varies considerably in sensitivity when comparing aromatics and halogenated methanes and ethanes. Halomethanes are approximately 20x less sensitive than aromatics and haloethanes approximately 10x less sensitive. Low-molecular-weight, water-soluble solvents (e.g., alcohols and ketones) will not extract from the water, and therefore will not be detected by GC/FID.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.0001 gm.

4.2 Gas Chromatograph: An analytical system complete with gas chromatograph suitable for on-column injection and all required accessories including syringes, analytical columns, gases, detector, and strip-chart recorder (or equivalent). A data system is recommended for measuring peak heights and/or peak areas.

4.2.1 **Detector:** Flame ionization (FID).

4.2.2 **GC column:** 3-m x 2-mm I.D. glass column packed with 10% OV-101 on 100/120 mesh Chromosorb W-HP (or equivalent). The column temperature should be programmed from 80°C to 280°C at 16°C/min and held at 280°C for 10 min.

4.3 Centrifuge: Capable of accommodating 50-mL glass tubes.

4.4 Vials and caps: 2-mL for GC autosampler.

4.5 Volumetric flasks: 10- and 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.6 Centrifuge tubes: 50-mL with ground-glass stopper or Teflon-lined screw-cap.

4.7 Pasteur pipets: Disposable.

4.8 Bottles: Teflon-sealed screw-cap.

5.0 REAGENTS

5.1 Hexadecane and methanol: Pesticide quality or equivalent.

5.2 Reagent water: Reagent water is defined as water in which an interference is not observed at the method detection limit of each parameter of interest.

5.3 Stock standard solutions (1.00 ug/uL): Stock standard solutions can be purchased as certified solutions or can be prepared from pure standard materials.

5.3.1 Prepare stock standard solutions by accurately weighing about 0.0100 grams of pure material. Dissolve the material in methanol in a 10-mL volumetric flask and dilute to volume (larger volumes may 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 available stock standards may be used if they are certified by the manufacturer.

5.3.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. These standards should be checked frequently for signs of degradation or evaporation.

5.4 Standard mixture #1: Standard mixture #1 should contain benzene, toluene, ethyl benzene, and xylene. Prepare a stock solution containing these compounds as described in Paragraph 5.3 and then prepare a working standard (through dilution) in which the concentration of each compound in the standard is 100 ng/uL in methanol.

5.5 Standard mixture #2: Standard mixture #2 should contain n-nonane and n-dodecane. Prepare a stock solution containing these compounds as described in Paragraph 5.3. Dilute the stock standard with methanol so that the concentration of each compound is 100 ng/uL.

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 preparation:

7.1.1 Water:

7.1.1.1 Allow the contents of the 40-mL sample vial to come to room temperature. Quickly transfer the contents of the 40-mL vial to a 50-mL volumetric flask. Immediately add 2.0 mL of hexadecane, cap the flask, and shake the contents vigorously for 1 min. Let phases separate. Open the flask and add sufficient reagent water to bring the hexadecane layer into the neck of the flask.

7.1.1.2 Transfer approximately 1 mL of the hexadecane layer to a 2.0-mL GC vial. If an emulsion is present after shaking the sample, break it by:

1. pulling the emulsion through a small plug of Pyrex glass wool packed in a pipet, or

2. transferring the emulsion to a centrifuge tube and centrifuging for several min.

7.1.2 Standards:

7.1.2.1 Add 200 uL of the working standard mixtures #1 and #2 to separate 40-mL portions of reagent water. Follow the instructions in Sections 7.1.1.1 and 7.1.1.2 with the immediate addition of 2.0 mL of hexadecane.

7.1.3 Sediment/Soil:

7.1.3.1 Add approximately 10 g of sample (wet weight) to 40 mL of reagent water in a 50-mL centrifuge tube. Cap and shake vigorously for 1 min. Centrifuge the sample briefly. Quickly transfer the supernatant water to a 50-mL volumetric flask.

7.1.3.2 Follow the instructions given in Sections 7.1.1.1 and 7.1.1.2, starting with the addition of 2.0 mL of hexadecane.

7.2 Analysis:

7.2.1 Calibration:

7.2.1.1 External standard calibration: The GC/FID must be calibrated each 12-hour shift for half of full-scale response when injecting 1-5 uL of each extracted standard mixture #1 and #2 (Paragraphs 5.4 and 5.5).

7.2.2 **GC/FID analysis:** Inject the same volume of hexadecane extract for the sample under investigation as was used to perform the external standard calibration. The GC conditions used for the standards analysis must also be the same as those used to analyze the samples.

7.2.3 **Interpretation of the GC/FID chromatograms:** There are two options for interpretation of the GC/FID results.

7.2.3.1 Option A: The standard mixture #1 is used to calculate an approximate concentration of the aromatics in the sample. Use this information to determine the proper dilution for purge-and-trap if the sample is a water. If the sample is a sediment/soil, use this information to determine which GC/MS purge-and-trap method (low- or high-level) should be used. If aromatics are absent from the sample or obscured by higher concentrations of other purgeables, use Option B.

7.2.3.2 Option B: The response of standard mixture #2 is used to determine which purge-and-trap method should be used for analyzing a sample. All purgeables of interest have retention times less than the n-dodecane retention time. A dilution factor (Paragraph 7.2.4.1.3) may be calculated for water samples, and an X factor (Paragraph 7.2.4.2.3) for soil/sediment samples, to determine whether the low- or high-level purge-and-trap procedure should be used.

7.2.4 Analytical decision point:

7.2.4.1 Water samples: Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.1.1 If no peaks are noted, analyze a 5-mL water sample by the purge-and-trap method.

7.2.4.1.2 If peaks are present prior to the n-dodecane peak and aromatics are distinguishable, follow Option A (Paragraph 7.2.3.1).

7.2.4.1.3 If peaks are present prior to the n-dodecane but the aromatics are absent or indistinguishable, Option B should be used as follows: If all peaks (prior to n-dodecane) are $<3\%$ of the n-nonane, analyze 5 mL of water sample by the purge-and-trap method. If any peak is $>3\%$ of the n-nonane, measure the area of the major peak and calculate the necessary dilution factor as follows:

$$\text{dilution factor} = 50 \times \frac{\text{area of major peak in sample}}{\text{peak area of n-nonane}}$$

The water sample should be diluted using the calculated factor just prior to purge-and-trap GC or GC/MS analysis.

7.2.4.2 **Soil/sediment samples:** Compare the hexadecane sample extract chromatograms against an extracted standard chromatogram.

7.2.4.2.1 If no peaks are noted, analyze a 5-g sample by the low-level purge-and-trap procedure.

7.2.4.2.2 If peaks are present prior to the n-dodecane and aromatics are distinguishable, follow Option A using the concentration information given in Table 1 to determine whether to analyze the sample by a low- or high-level purge-and-trap technique.

7.2.4.2.3 If peaks are present prior to n-dodecane but aromatics are absent or indistinguishable, use Option B. Calculate an X factor for the sample using the following equation:

$$X \text{ factor} = \frac{\text{area of major peak in sample}}{\text{area of n-nonane}}$$

Use the information provided in Table 1 to determine how the sample should be handled for GC/MS analysis.

7.2.4.2.4 If a high-level method is indicated, the information provided in Table 2 can be used to determine the volume of methanol extract to add to 5 mL of reagent water for analysis (see Methods 5030 and 8240 for methanolic extraction procedure).

8.0 QUALITY CONTROL

8.1 It is recommended that a reagent blank be analyzed by this screening procedure to ensure that no laboratory contamination exists. A blank should be performed for each set of samples undergoing extraction and screening.

9.0 METHOD PERFORMANCE

9.1 No data available.

10.0 REFERENCES

1. U.S. EPA Contract Laboratory Program, Statement of Work for Organic Analysis, July 1985, Revision.

TABLE 1. DETERMINATION OF GC/MS PURGE-AND-TRAP METHOD

X Factor	Approximate Concentration Range [a]	Analyze by
0-1.0	0-1,000 ug/kg	Low-level method
>1.0	>1,000 ug/kg	High-level method

[a] This concentration range is based upon the response of aromatics to GC/FID. The concentration for halomethanes is 20x higher, and haloethanes 10x higher, when comparing GC/FID responses.

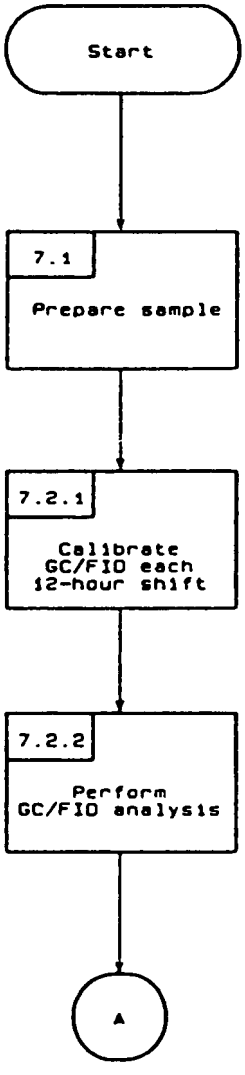
TABLE 2. QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-LEVEL SOIL/SEDIMENTS

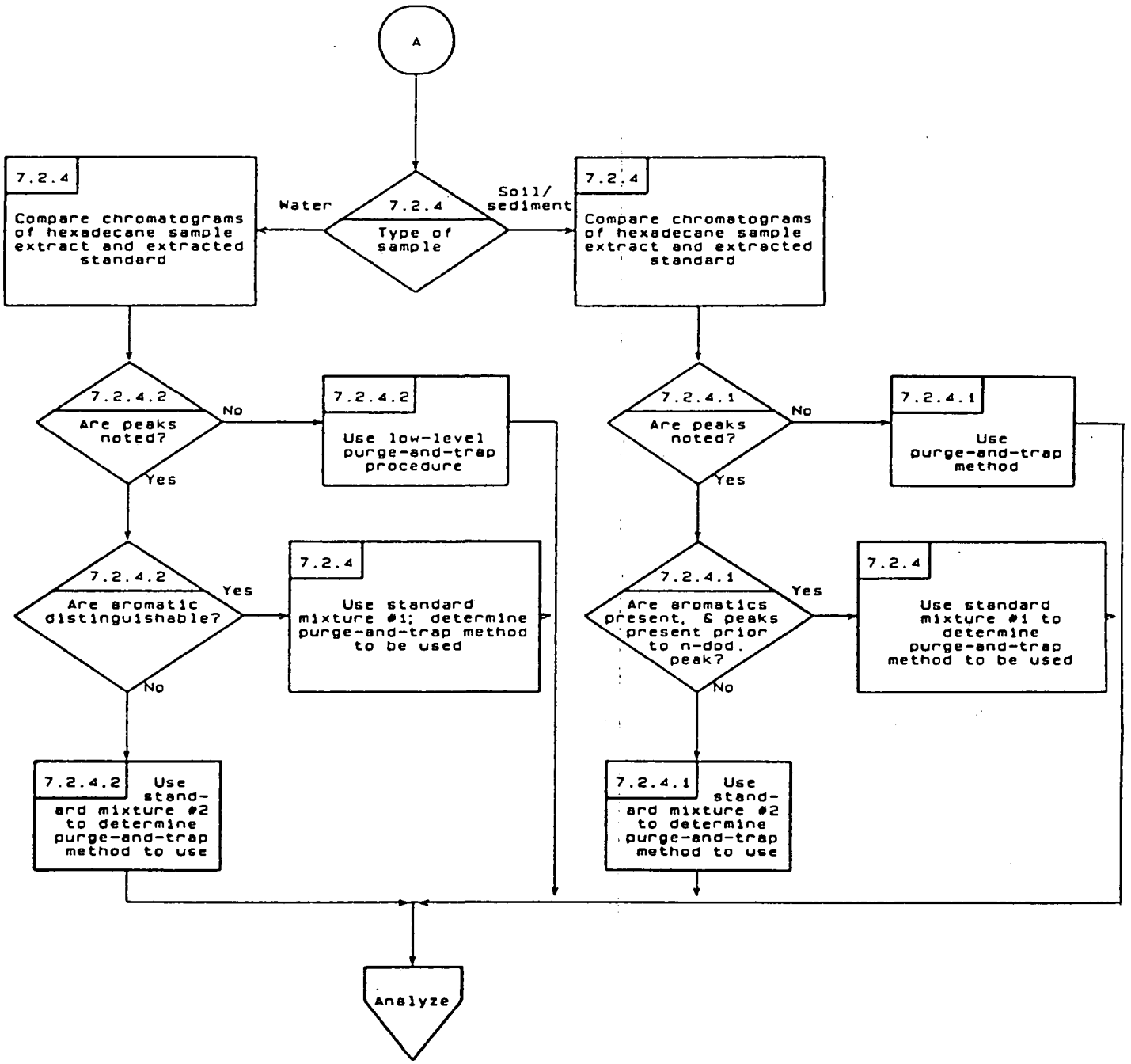
X Factor	Approximate Concentration Range [a]	Volume of Methanol Extract [b]
0.25-5.0	500-10,000 ug/kg	100 ul
0.5-10.0	1,000-20,000 ug/kg	50 ul
2.5-50.0	5,000-100,000 ug/kg	10 ul
12.5-250	25,000-500,000 ug/kg	100 uL of 1/50 dilution [c]

[a] Actual concentration ranges could be 10 to 20 times higher than this if the compounds are halogenated and the estimates are from GC/FID.

[b] The volume of methanol added to 5 mL of water being purged should be 100 uL. Therefore if the amount of methanol extract required is less than 100 uL, additional methanol should be added to maintain the constant 100-uL volume.

[c] Dilute an aliquot of the methanol extract and then take 100 uL for analysis.


Start
7.1
Prepare sample
7.2.1
Calibrate GC/FID each 12-hour shift
7.2.2
Perform GC/FID analysis
A


A
7.2.4
Type of sample
Water
Soil/ sediment
7.2.4
Compare chromatograms of hexadecane sample extract and extracted standard
7.2.4
Compare chromatograms of hexadecane sample extract and extracted standard
7.2.4.2
Are peaks noted?
No
Yes
7.2.4.2
Use low-level purge-and-trap procedure
7.2.4.2
Are aromatic distinguishable?
Yes
No
7.2.4
Use standard mixture #1; determine purge-and-trap method to be used
7.2.4.2
Use standard mixture #2 to determine purge-and-trap method to use
7.2.4.1
Are peaks noted?
No
Yes
7.2.4.1
Use purge-and-trap method
7.2.4.1
Are aromatics present, & peaks present prior to n-dod. peak?
Yes
No
7.2.4
Use standard mixture #1 to determine purge-and-trap method to be used
7.2.4.1
Use standard mixture #2 to determine purge-and-trap method to use
Analyze

APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

Revision 0
Date September 1986

☆ U.S. GOVERNMENT PRINTING OFFICE : 1987 O - 169-932